Research Letter

Homogenization of Mutually Immiscible Polymers Using Nanoscale Effects: A Theoretical Study

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A theoretical study to investigate homogenization of mutually immiscible polymers using nanoscale effects has been performed. Specifically, the miscibility behavior of all-polymer nanocomposites composed of linear-polystyrene (PS) chains and individual cross-linked poly(methyl methacrylate)-nanoparticles (PMMA-NPs) has been predicted. By using a mean field theory accounting for combinatorial interaction energy and nanoparticle-driven effects, phase diagrams were constructed as a function of PMMA-NP size, PS molecular weight, and temperature. Interestingly, complete miscibility (i.e., homogeneity) was predicted from room temperature to 675 K for PMMA-nanoparticles with radius less than $\sim$7 nm blended with PS chains (molecular weight 150 kDa, nanoparticle volume fraction 20%) in spite of the well-known immiscibility between PS and PMMA. Several nanoscale effects affecting miscibility in PMMA-NP/PS nanocomposites involving small PMMA-nanoparticles are discussed.

1. INTRODUCTION

Nanoscale effects are responsible for the growing scientific interest in both nanomaterials and nanocomposites [1]. Often, nanoobjects display interesting physical phenomena such as surface plasmon resonance in metallic nanoparticles (NPs), ballistic transport in carbon nanotubes (CNTs), or fluorescence emission in quantum dots (QDs), among others. Most of them are useful for a huge of potential applications covering from nanoelectronic to improved sensors devices [2]. Also, nanocomposites composed of well-dispersed nanoobjects into a polymer matrix lead to unexpected mechanical [3] and/or rheological properties [4]. A representative example is the large decrease (up to 80%) in melt viscosity upon nanoparticle addition first observed in polystyrene-nanoparticle (PS-NP)/linear-polystyrene (PS) blends by Mackay et al. [5]. The underlying physics of this unexpected behavior is being currently explored [6] and should be rationalized in terms of scaling concepts at the nanoscale [7]. Blend miscibility (homogeneity) is a necessary condition to observe such a viscosity drop in *all-polymer nanocomposites* (i.e., polymer-nanoparticle/linear-polymer blends).

Recently, we have introduced an entropic model for predicting the miscibility behavior of PS-NP/PS nanocomposites with very good agreement between theory and experiment [8]. Additionally, the theory has been employed for the prediction of the interaction parameter, the miscibility behavior, and the melting point depression of athermal poly(ethylene) (PE)-nanoparticle/linear-PE nanocomposites using chain dimensions data from Monte-Carlo (MC) simulations [9]. Our main findings indicate that dilution of contact, hard sphere-like, nanoparticle-nanoparticle interactions plays a key role in explaining the miscibility behavior of polymer-nanoparticles dispersed in a chemically identical linear-polymer matrix [8, 9].

In a recent work, the athermal model has been extended to calculate the phase diagram of weakly interacting all-polymer nanocomposites by accounting for combinatorial interaction energy and nanoparticle-driven effects [10]. Complete miscibility was predicted for PS-nanoparticles with radius < 6 nm blended with poly(vinyl methyl ether) (PVME) at low concentrations. When compared to linear-PS/PVME blends displaying phase splitting at $T > 375$ K, the miscibility improving effect of sub-10 nm PS-nanoparticles was clearly highlighted [10].

In this letter, we explore theoretically the conditions for homogenization of two mutually immiscible polymers by changing all the linear-polymer chains of one of the components by cross-linked polymer nanoparticles. Specifically, we consider the PS/poly(methyl methacrylate) (PMMA) pair as a model system. Immiscibility between PS and PMMA is well known in the literature as a result of unfavorable interactions between styrene (S) and methyl methacrylate (MMA) repeat units [11–13]. Here, miscibility diagrams for PMMA-NP/PS nanocomposites are reported as a function of PMMA-NP size, PS molecular weight (M_n) and temperature. Finally, several nanoscale effects affecting the miscibility behavior of PMMA-NP/PS nanocomposites are also discussed.

2. THEORETICAL APPROACH

For a binary blend to be thermodynamically stable against phase separation, the following well-known conditions must be fulfilled:

$$\Delta g_{\text{mix}} < 0,$$
$$\Delta g_{\text{mix}}^{(2)} \equiv \left(\frac{\partial^2 \Delta g_{\text{mix}}}{\partial \phi_1^2} \right) > 0. \tag{1}$$

In a mean field, theoretical framework, Δg_{mix}, the free energy of mixing (per unit volume) for an all-polymer nanocomposite composed of spherical polymer-nanoparticles (component 1) of volume fraction ϕ_1, radius R_p, nanoparticle volume v_1, and linear-polymer chains of degree of polymerization $N_2(\gg 1)$ and monomer volume v_2 is given by [10]

$$\Delta g_{\text{mix}} = \Delta g_{\text{mix}}^{\text{co}} + \Delta g_{\text{mix}}^{\text{np}} + \Delta g_{\text{mix}}^{\text{ex}}, \tag{1}$$

$$\Delta g_{\text{mix}}^{\text{co}} = kT \left[\frac{\phi_1}{v_1} \ln \phi_1 + \frac{\phi_2}{N_2 v_2} \ln \phi_2 \right], \tag{1a}$$

$$\Delta g_{\text{mix}}^{\text{np}} = kT \left[\frac{\phi_1}{v_1} \left(\frac{4\phi_1 - 3\phi_1^2}{(1 - \phi_1)^2} \right) + \frac{3}{2} \times \frac{\phi_1 \phi_2}{N_2 v_2} \left(\frac{R_p}{R_{g2}} \right)^2 \right], \tag{1b}$$

$$\Delta g_{\text{mix}}^{\text{ex}} = \left(\frac{r_2}{R_p} \right) \left[\frac{kT}{v_2} \left(\chi_S + \frac{\chi_H}{T} \right) \right] \phi_1 \phi_2, \tag{1c}$$

where k is the Boltzmann constant, T is the absolute temperature, R_{g2} is the radius of gyration of linear-polymer 2, r_2 is the radius of a repeat unit 2, and χ_S and χ_H are the entropic and enthalpic components of the blend interaction parameter ($\chi = \chi_S + \chi_H/T$), respectively.

Equation (1a) provides the contribution to the total free energy of mixing due to the *combinatorial entropy* of mixing, whereas (1b) gives the contribution to the free energy of mixing due to *nanoparticle-driven* effects. Equation (1b) takes into account the dilution of hard sphere-like nanoparticle-nanoparticle interactions upon mixing (first RHS term) [8, 9] and the stretching of the linear-polymer chains due to the presence of the nanoparticles (second RHS term). Referring to this latter term, a Ginzburg-type expansion term is adopted to account for the fact that the polymer-nanoparticles cause stretching of the polymer chains in their vicinity [14].

Equation (1c) accounts for the temperature-dependent and nanoparticle size-dependent *interaction* effects in the all-polymer nanocomposite. A prefactor (r_2/R_p) is introduced in (1c) since the number of surface contacts with monomers 2 for each nanoparticle becomes smaller as one increases the nanoparticle radius [14]. This ratio tends toward unity inasmuch $R_p \to r_1$ as it should, r_1 being the radius of a repeat unit 1.

For the sake of simplicity, in (1) we have omitted a term ($\sim$constant$\times\phi_1$) arising from the (non-zero) reference free energy of the pure component 1 in the disordered molten state at $\phi_1^{\text{fr}} = 0.494$ (maximum packaging of monodisperse spheres) as dicussed in [9] which has no effect in the resulting spinodal equation (second derivative of the free energy of mixing with respect to ϕ_1).

The condition $\Delta g_{\text{mix}}^{(2)} = 0$ just determines the spinodal miscibility boundary in the phase diagram, which is given by

$$\Delta g_{\text{mix}}^{(2)} = \Delta g_{\text{mix}}^{\text{co}(2)} + \Delta g_{\text{mix}}^{\text{np}(2)} + \Delta g_{\text{mix}}^{\text{ex}(2)} = 0, \tag{2}$$

$$\Delta g_{\text{mix}}^{\text{co}(2)} = kT \left[\frac{1}{v_1 \phi_1} + \frac{1}{N_2 v_2 \phi_2} \right], \tag{2a}$$

$$\Delta g_{\text{mix}}^{\text{np}(2)} = kT \left[\frac{2}{v_1} \left(\frac{4 - \phi_1}{(1 - \phi_1)^4} \right) - \frac{9}{2v_2} \left(\frac{R_p}{r_2 N_2} \right)^2 \right], \tag{2b}$$

$$\Delta g_{\text{mix}}^{\text{ex}(2)} = -2 \left(\frac{r_2}{R_p} \right) \left[\frac{kT}{v_2} \left(\chi_S + \frac{\chi_H}{T} \right) \right], \tag{2c}$$

where we have employed $R_{g2} \approx 2r_2 N_2^{1/2}/\sqrt{6}$.

Equations (1)–(2) are presumably valid only for $\phi_1 < 0.494$ (the theoretical maximum nanoparticle packaging volume fraction without freezing) and for $R_p > \sim 5r_2$ (it should be noted that r_2 is typically around 0.3 nm) [10].

3. RESULTS AND DISCUSSION

It is well known that PS and PMMA lead to heterogeneous (phase separated) blends due to the immiscibility between components at high molecular weights [11–13]. The S/MMA temperature-dependent interaction parameter ($\chi = \chi_S + \chi_H/T$) has been determined by several experimental techniques such as small angle neutron scattering (SANS) (using deuterated block copolymers) [11, 12] and cloud-point (CP) measurements (using oligomer mixtures and taking into account end-group effects) [13] with good agreement between them. As an example, $\chi = 0.028 + 3.9/T$ by SANS measurements [11] and $\chi = 0.021 + 2.8/T$ by CP experiments [13]. Since the entropic contribution, χ_S, is much greater than the (χ_H/T) term, the temperature dependence of χ was found to be relatively weak.

We have employed the temperature-dependent interaction parameter determined by CP measurements to calculate the spinodal miscibility boundary of PMMA-NP/PS composites as a function of nanoparticle radius at constant blend composition (see Figure 1). Complete miscibility across the 275–675 K temperature range was predicted for PMMA-nanoparticles with radius less than 6.8 nm in spite of the well-known immiscibility between PMMA and PS
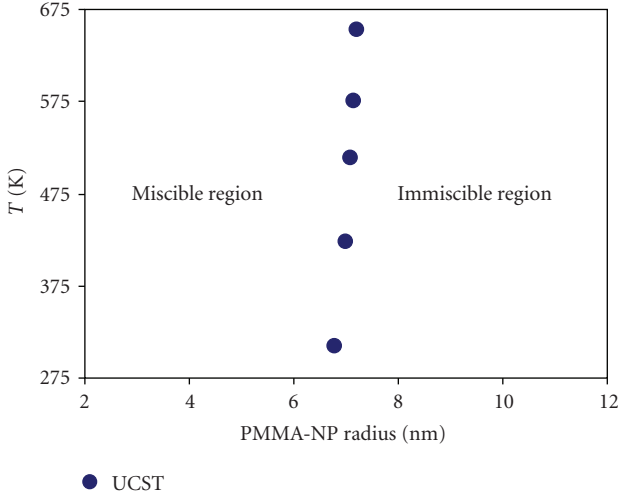
FIGURE 1: Predicted phase diagram for PMMA-NP/PS (M_n = 150 kDa) nanocomposites as a function of nanoparticle size as calculated from (2) by using $\chi = 0.021 + 2.8/T$ [13], $\phi_1 = 0.2$, $N_2 = 1443$, $v_2 = 99\,\text{cm}^3/\text{mol}$, and $r_2 = 0.32\,\text{nm}$.
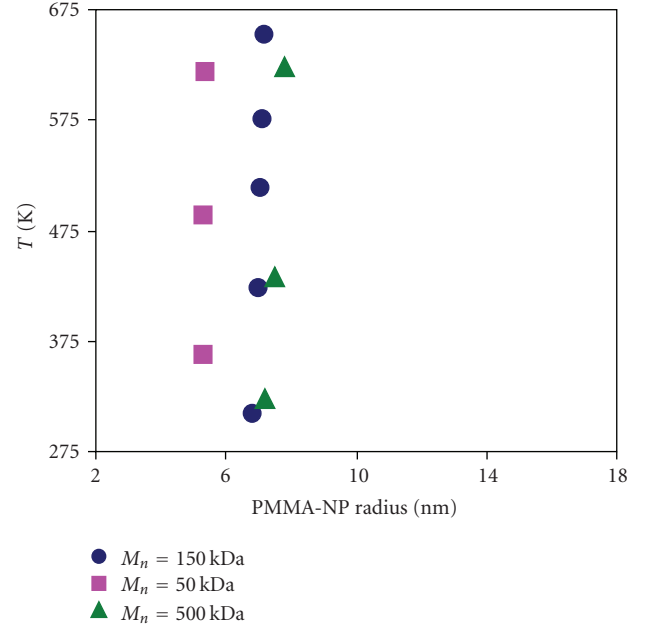

FIGURE 2: Influence of PS molecular weight on the calculated phase diagram for PMMA-NP/PS nanocomposites ($\phi_1 = 0.2$): M_n = 50 kDa (solid squares), $M_n = 150$ kDa (solid circles), and $M_n = 500$ kDa (solid triangles).

homopolymers. Conversely, for PMMA-nanoparticles with radius higher than 7.2 nm, complete immiscibility (phase separation) is expected. For PMMA-NP of radius in between 6.8 and 7.2 nm, partial miscibility was predicted as a function of temperature (the blends displaying upper critical solution temperature (UCST)-type behavior). No significant changes was observed when χ values from SANS experiments [11, 12] were employed in the calculations.

In order to rationalize these nanoscale-driven results, we have examined the values of the different factors governing (2) (second derivative of the energy of mixing). $\Delta g_{\text{mix}}^{\text{co}(2)}$ (arising from *combinatorial* effects) was found to be positive (favorable to mixing) and increased linearly with temperature. Conversely, $\Delta g_{\text{mix}}^{\text{ex}(2)}$ (arising from *interactions*) was negative and increased in absolute value with T. In general, $|\Delta g_{\text{mix}}^{\text{ex}(2)}| > \Delta g_{\text{mix}}^{\text{co}(2)}$ so miscibility was conditioned by favorable values of the $\Delta g_{\text{mix}}^{\text{np}(2)}$ term. At constant ϕ_1, the size of the PMMA-nanoparticles was the main factor affecting the $\Delta g_{\text{mix}}^{\text{np}(2)}$ term (see (2b)). At a given temperature, $\Delta g_{\text{mix}}^{\text{np}(2)}$ was found to decrease upon increasing the PMMA-NP size leading, respectively, to partial and complete immiscibility at PMMA-NP radius of 7 and 7.5 nm. As a result, miscibility in PMMA-NP/PS nanocomposites can be mainly attributed to two combined effects: (1) reduced (unfavorable) PS chain stretching by smaller PMMA-nanoparticles and (2) favorable dilution of (hard sphere-like) nanoparticle-nanoparticle interactions upon mixing.

The effect of PS molecular weight on the predicted phase diagram for PMMA-NP/PS nanocomposites is illustrated in Figure 2. As expected, a reduction in PS molecular weight shifts the miscibility boundary toward smaller nanoparticle sizes due to the large entropy penalty paid for nanoparticle inclusion into short linear-polymer chains. Hence, the critical PMMA-NP radius for complete immiscibility (R_p^C)

changes from 5.4 to 7.2 and 7.8 nm upon changing the PS molecular weight from 50 to 150 and 500 kDa, respectively.

Concerning the effect of blend composition on R_p^C for PMMA-NP/PS ($M_n = 150$ kDa) nanocomposites, a linear increase in R_p^C (up to ~29%) on going from $\phi_1 = 0.15$ ($R_p^C = 6.9$ nm) to $\phi_1 = 0.35$ ($R_p^C = 8.9$ nm) was observed.

4. CONCLUSIONS

A mean field theoretical model, accounting for combinatorial interaction energy and nanoparticle-driven effects, has been employed to investigate homogenization of mutually immiscible polymers using nanoscale effects. The PS/PMMA pair has been selected as a model system since immiscibility between PS and PMMA is well documented in the literature, and reliable values of the S/MMA interaction parameter are available as a function of T. Specifically, we have investigated the effect on blend miscibility (homogeneity) of the replacement of linear-PMMA chains by cross-linked individual PMMA-nanoparticles.

Hence, phase diagrams have been constructed for PMMA-NP/PS nanocomposites as a function of PMMA-NP size, PS molecular weight, blend composition, and temperature. Interestingly, complete miscibility across the 275–675 K temperature range was predicted for PMMA-nanoparticles with radius less than 6.8 nm blended with PS ($M_n = 150$ kDa, $\phi_1 = 0.2$). Increasing PS molecular weight and nanoparticle content was found to have a small positive effect on PMMA-NP/PS nanocomposite miscibility.

Homogenization of PMMA-NP/PS nanocomposites was mainly attributed to two combined nanoeffects: reduced PS

chain stretching by the smaller PMMA-nanoparticles, and favorable dilution of contact (hard sphere-like) nanoparticle-nanoparticle interactions upon mixing.

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