Effect of particle size on the phase behavior of block copolymer/nanoparticle composites

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1. Introduction

Heterogeneous materials comprising inorganic fillers in the length scale of nanometer and a soft matrix is one of the fastest growing areas of materials research. These hybrid materials possess the unique features of each constitutes and can facilitate the development of catalysts, selective membranes, and photonic band gap materials [1–7]. Recently, there has been great interest in tailoring the unique features of each constitutes and can facilitate the development of catalysts, selective membranes, and photonic band gap materials [8–26]. By the nature of the phase separation of the block copolymer [8–26], nanoparticles can self assemble into highly organized arrays. Such spatially regular nanocomposites could potentially be used in various nanotechnological applications exploiting their magnetic, optical, electrical and mechanical properties.

Tremendous progress has been reported to achieve a fundamental understanding of how the presence of nanoparticles affects the ordering of block copolymers. Theoretical approaches reveal that both entropy and enthalpy contributed from nanoparticles induce phase transformation [6,7,27–36]. By varying the particle size and concentration, the morphology of composites can be tuned to an ordered phase, the co-existence of particle-rich and block copolymer-rich phases, or new microphase-separated structures [27]. However, larger particles are less significant in reducing the order–disorder transition temperature than the smaller ones. In addition, by the combination of the self-consistent field theory for polymer and the density functional theory for particles to capture the features of this complicated system, the spatial organization of particles in the ordered phases was explored [6]. It was found that large particles tend to concentrate at the center of the preferred domains to maintain in the energetically more favorable status. On the contrary, small particles organize at the polymer interface to gain their maximum translational entropy. In addition to the specific particle size and chemistry that can engineer the morphology of block copolymer/nanoparticle composites, particle shape is also an important factor to influence the phase behavior of these composites. Chernyayev and Balazs [32] developed self-consistent equations to describe the particle shape effect on the order–disorder transitions in composites. It was found that spherocylinders with the smaller aspect ratio produce the bigger effect on the transitions.

On the experimental front, many recent studies have developed approaches to manipulate the rich phase behavior of block copolymer by the incorporation of functionalized nanoparticles...
into polymer matrices. The resulting morphology showed a strong function of particle concentration [24,37–42]. Lo et al. [23,26] demonstrated systematic studies on the phase behavior of block polymer/nanoparticle composites. The results revealed the swelling and the increase in the interfacial curvature upon the addition of nanoparticles within the preferred domains of block copolymer induces order–order transitions. With increasing particle loading, nanoparticles enhance the local compositional fluctuations that increase the interfacial roughness between two domains, causing order–disorder transitions. At high particle loading, packing constraint excludes excess particles from the preferred domains, leading to macrophase separation. Size and shape, packing constraint excludes excess particles from the preferred domains, causing order–disorder transitions. At high particle load-

<table>
<thead>
<tr>
<th>$M_\text{c}$ of PSSH (g/mol)</th>
<th>$R_g$ (nm)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>1.0</td>
<td>6.2</td>
</tr>
<tr>
<td>3000</td>
<td>1.5</td>
<td>7.2</td>
</tr>
<tr>
<td>5300</td>
<td>2.0</td>
<td>8.2</td>
</tr>
<tr>
<td>12,000</td>
<td>2.9</td>
<td>10.0</td>
</tr>
</tbody>
</table>

collected and re-dispersed in chloroform ($\geq99.8\%$, J.T. Baker). An equimolar volume of thiol-terminated polystyrene (PSSH, Polymer Source, Inc.) was then mixed with particle solution, and stored at ambient condition for 3 days. Pd nanoparticles were purified by ethanol ($\geq99.5\%$, J.T. Baker) to obtain PSSH-tethered Pd nanoparticles. The surface treatment of Pd nanoparticles using PSSH is to ensure the selective incorporation of particles into the PS domains of PS-PVPH and prevent particles from aggregation.

As-prepared Pd nanoparticles were mixed with PS-PVPH with total molecular weights, $M_n$, of 80.5 kg/mol (PS-PVPH-80.5K, $f_{PS} = 0.50$, PDI = 1.10, Polymer Source, Inc.) and 16.5 kg/mol (PS-PVPH-16.5K, $f_{PS} = 0.50$, PDI = 1.09, Polymer Source, Inc.) in toluene ($\sim100\%$, J.T. Baker), respectively, to prepare PS-PVPH/nanoparticle composites. The complex solution was stored at ambient condition for at least 3 days, and then cast on both epoxy resin and aluminum pan to make bulk composite. After drying in vacuum, the specimen was annealed at 180 °C for 1 week.

2.2. Transmission electron microscopy (TEM)

An Ultracat R microtome (Reichert, Leica, MI) was used to section the embedded samples in epoxy to a thickness of $\sim80$ nm. To enhance the contrast between PS and PVP domains, specimens were stained by iodine vapor for 24 h. Iodine adsorbs to PVP that reveals as dark regions in TEM. The morphology of composites was then characterized using a Hitachi H7500 transmission electron microscope operated at 100 kV. Additionally, nanoparticles were observed using a JEOL JEM-3000F microscope under an accelerating voltage of 300 kV.

2.3. Differential scanning calorimetry (DSC)

The thermal properties of composites were measured using a scanning differential calorimeter (DSC 7, Perkin Elmer). Samples of $\sim5$ mg were heated from 25 °C to 140 °C with a heating rate of 10 °C/min to reveal the effect of particles on the glass transition temperature ($T_g$) of composites.

3. Results and discussion

3.1. The characterization of Pd nanoparticles

Table 1 shows the diameter of Pd nanoparticles before grafted with PSSH. The average diameter of particles is $\sim4.2$ nm. Further treatment of particle surface using PSSH enables the assembly of particles in the PS domains of PS-PVPH. It has been proposed that the size of particles plays an important role on the phase behavior of block copolymer/nanoparticle composites. In our work, both Pd and tethered PSSH chains contribute to the total size of particles. The shell thickness of PSSH can be approximated by the radius of gyration of PSSH ($R_g$), given by [46]

$$ R_g = \sqrt{\frac{N}{6} b} $$

where $N$ is the degree of polymerization of PSSH and $b$ is the Kuhn segment length, taken as 6.7 Å [47].
Acknowledgements

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References


