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Surface Segregation of Nanoparticles Driven by Supercritical Carbon Dioxide

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Abstract. Surface segregation (i.e., preferential segregation of one component to the surface in multicomponent systems) is common to all material classes and is typically driven by a reduction in surface energy which compensates for the entropy loss and/or energy gain associated with the demixing of the components. However, the conventional surface segregation for polymeric systems requires high temperatures, typically close to 200°C, and long annealing time, in order to ensure enough polymer mobility. Here we show a low-temperature method to preferentially migrate organoclay nanoparticles to the polymer surface using supercritical carbon dioxide.

1. Introduction

The self-assembly of nanoparticles is an attractive approach for nanostructure fabrication. The control of layered structures on the nanometer scale is particularly desirable for thin-film organic devices, because this essentially affects the electrical, optical, and mechanical properties. To spontaneously fabricate such layered structures, careful control of driving forces such as phase separation, crystallization, or surface energy of materials is necessary. Krishan et al. reported a new means to obtain self-assembled multilayer structures at the nanometer level: the counterbalance between the conformational entropy gain of moving the linear polymer chain away from the substrate and mixing enthalpy and translational entropy losses of the nanoparticles by moving to the substrate interface [1]. Recently, Wei et al. synthesized a fullerene (C₆₀) derivative with a fluorocarbon chain, which has a low surface energy and prefers to migrate to the air/polymer interface during spin-coating process, and could create a very thin layer of the nanoparticles at the polymer/air interface to be used for organic thin film transistors [2]. Although these studies propose new attractive methods for fabrication of various organic thin-film devices, their applications to actual electronic devices are still very limited and remain challenging. In this paper, with the aim of developing a new route to control the self-assembling process of nanoparticles embedded in polymer thin films, we describe simple and effective surface modifications applicable to a wide variety of polymer nanocomposite films using supercritical carbon dioxide (scCO₂, the critical point is $T_c = 31.3$ °C and $P_c = 7.38$ MPa). ScCO₂ is being used increasingly as an environmentally friendly solvent for polymer processing and synthesis [3]. The

novel temperature and pressure conditions near the critical point where the anomalous absorption of CO₂ molecules into “CO₂-phobic” polymer thin films [4] were utilized in the study.

2. Experimental

A polymer examined for this study was monodisperse polystyrene (PS, Pressure Chemical Co., weight average molecular weight (M_w) = 200,000, polydispersity index = 1.06). Organoclay particle (Cloisite 6A, a natural montmorillonite with alkyl *N, N*-dimethyl dehydrogenated tallow quaternary ammonium chloride) was used as a model. The nanoparticle was firstly dissolved in toluene and the polymer was then added to the solution. The weight fraction of the clay nanoparticles against the polymer was 0.01. The solutions were sonicated for 60 seconds prior to spin-coating process in order to prevent from aggregation of the nanoparticles. The surface free energies of PS and clay are 33 and 30-35 mJm⁻², respectively. The polymer nanocomposite films without pre-annealing at high temperature were then placed in the high pressure cell [5] and immersed in scCO₂ under the unique condition of $T = 36$ °C and $P = 8.2$ MPa, where the anomalous swelling of various polymer thin films was induced by long-range density fluctuations (hereafter we call the T and P condition as the “ridge” condition). We also examined the surface structures of the pre-annealed films at $T = 170$ °C in vacuum for 2 h as controls. Surface morphologies of all the films were observed by an atomic force microscope (AFM) and lateral force microscope (LFM) (Digital Instruments, Dimension 3100) with a silicon nitride cantilever. The images obtained were then analyzed by using ImageJ 1.40g software (NIH, USA).

3. Results and Discussion

Fig. 1(a) and 1(b) present the topographic surface morphologies of the as-spun and thermally annealed PS/clay thin films measured by AFM. We can see that the film annealed at $T = 170$ °C in vacuum for 2 h has a rough surface, while the surface of the original as-spun film is relatively flat. Fig. 1(d) and 1(e) correspond to the cross-sectional profiles of Fig. 1(a) and 1(b), respectively, indicating that the dewetting takes place during the annealing process. From the X-ray reflectivity measurement for the as-spun PS/clay film, we observed the monolayer formation of the clay particles at the substrate, indicating that the strong affinity of the clays for a native oxide layer and the dewetting is caused by the poor interaction between the clay particle and PS [6]. Fig. 1(c) and 1(f) are the surface morphologies of the scCO₂ treated PS/clay thin film at the ridge condition and its cross-sectional profile, respectively. Interestingly, no dewetting was observed even after 23 h exposure time in scCO₂ and rather the surface became rougher due to the segregation of the clay particle (the bright spots in the AFM images correspond to the clay nanoparticles).

In order to quantitatively characterize the surface segregation structures of the clay nanoparticles, we conducted an image analysis on the LFM pictures, which offer a frictional force contrast on a surface. This

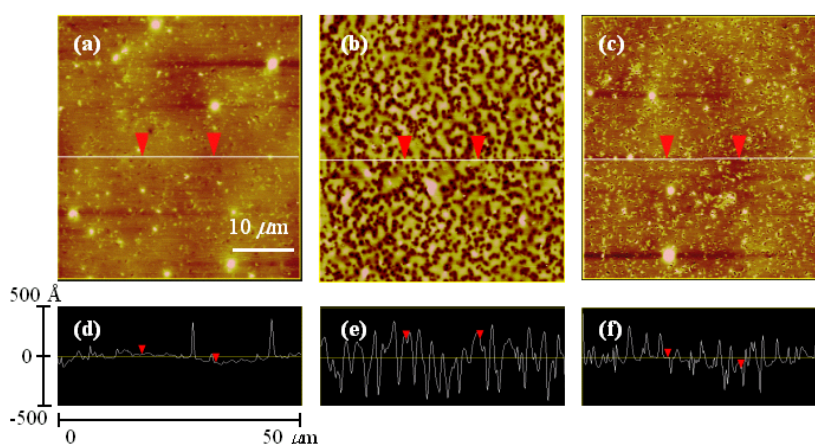


Figure 1. Topographic images for the (a) as-spun, (b) thermally annealed ($T = 170$ °C for 24 h in vacuum) and (c) CO₂ treated ($P = 8.2$ MPa and $T = 36$ °C for 1 h) PS/clay thin films. The scan sizes and height scales for the images are $50 \times 50 \mu\text{m}^2$ and 0-1000 Å, respectively. (d), (e) and (f) show the cross-sectional profiles along the white lines in (a), (b) and (c), respectively. The height scales for these profiles are 0-1000 Å.

allows us to quantify the surface exposing clay nanoparticles with relatively large difference in the frictional nature. The calculated areas of the surface exposing clays in the PS/clay thin film (both 50 and 100 nm thickness) are presented in Fig. 2. For the as-spun films of both 50 and 100 nm in thick, approximately 7.5 % in topmost area was covered by the clay particles. On the other hand, the surface coverage of the particles after exposing to scCO₂ increased up to more than 10 % for both films, which corresponds to an approximately 40 % increase from the unexposed film. Hence, it is obvious that the scCO₂ treatment induces the surface segregation of the particles. From the figure we see no significant time dependence of the surface exposed clay nanoparticles after 1 h exposure, suggesting the surface segregated structure is an equilibrium state. In addition, we also found that the observed surface segregation is very sensitive to employed *T* and *P* conditions; it can take place only at the ridge condition, indicating that the density fluctuating scCO₂ is a key for the phenomenon.

We also investigated polyhedral oligomeric silsesquioxane nanoparticles co-polymerized with styrene monomers (the weight fraction of the POSS component was 15%) embedded in the same PS matrix by using AFM and neutron reflectivity and found similar surface segregation of the nanoparticles after the same scCO₂ treatment. Hence, it is clear that the enthalpic interactions are not the central driving force for the scCO₂-induced surface migration. Rather, an entropic effect imposed on the polymer chains owing to the presence of the nanoparticles would be crucial. As the individual polymer chains must extend and stretch around the nanoparticles to achieve the equilibrium swelling in scCO₂, there is an entropic gain in expelling the nanoparticles to the free surface, as previously reported for surface segregation of nanoparticles at the air/polymer interface [7]. Another important factor would be the critical wetting of CO₂ molecules onto nanoparticle surfaces in the highly compressible region [8]. These combined effects could push the nanoparticles out of the film even though the nanoparticles are ‘soluble’ in the polymer matrix.

4. Conclusion

In summary, we have described a very simple, yet robust approach to induce the surface segregation of nanoparticles by using supercritical CO₂ under the unique *T* and *P* condition. The resultant surface structures can be then preserved by the vitrification of the polymer chains via rapid pressure quenching. Hence, this experimental finding would facilitate the use of scCO₂ as a low-temperature and environmentally friendly solvent for creating a variety of nano-patterned polymer surfaces tailored to one’s needs.

Acknowledgements

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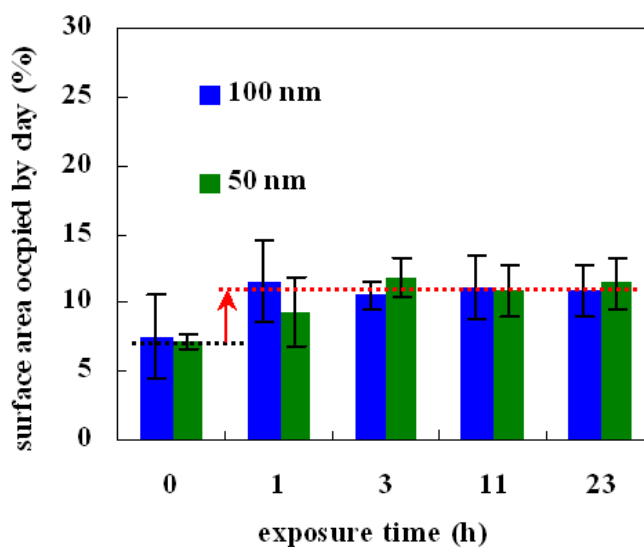


Figure 2. Calculated surface areas occupied by the clay nanoparticles as a function of CO₂ exposure time.

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