

Spinodal clustering induced dewetting and non-monotonic stabilization of polymer blend films at high nanofiller concentrations



Diya Bandyopadhyay^{a,1}, Danielle Grolman^a, Gurpreet Singh^{a,2}, Jack F. Douglas^{b,3}, Alamgir Karim^{a,*}

^a Department of Polymer Engineering, The University of Akron, Akron, OH 44325, United States

^b Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

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ABSTRACT

We examine the effects of high fullerene nanoparticle (f-NP) concentrations, $\phi_{f-NP} \sim (10-20)$ mass% on polystyrene (PS)/polybutadiene (PB) blend thin film stability. Dewetting of the polymer blend around spinodally clustered f-NPs in this high concentration limit leads to a spinodal like dewetting morphology. This is in contrast to our previously observed results on the stabilization effects of f-NPs on PS/PB blend thin films in the intermediate f-NP concentration range of 7–10 mass%, wherein, after saturating the polymer–blend interface, the NPs stabilize the film by segregating to the blend–substrate interface. We determine three regimes of polymer blend film stability as a function of filler concentration: a) $\phi_{f-NP} < 7$ mass% where preferential segregation of the f-NPs to the polymer–polymer interface leads to macroscopic dewetting, b) $\phi_{f-NP} \sim (7-10)$ mass% where PS/PB blend films exhibit complete film stability, and c) $\phi_{f-NP} \sim (11-20)$ mass%, where spinodal clustering of the f-NPs gives rise to polymer–NP phase exclusion and subsequent dewetting.

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1. Introduction

Morphology evolution in nanoparticle (NP)-filled phase separating polymer blend films is expected to depend upon how the NP dispersion and clustering interacts with the composition fluctuations of the phase separating polymer blend, in conjunction with the polymer–substrate–NP interactions that affects thin film stability against dewetting [1]. Simulation studies using the Cahn–Hilliard–Cook model for blends have shown that in the presence of nanofillers, selective affinity of one of the polymer components towards the NP surface gives rise to preferential wetting driven concentration waves about the filler clusters that transition to characteristic spinodal patterns due to simultaneous blend phase separation [2]. Recently, Cabral et al. have shown that for high molecular mass homopolymer PS ($M_w \sim 10,000-270,000$ g/mol)–C₆₀ mixtures, at C₆₀ concentrations above 5 mass% NP, formation of spinodal surface undulations analogous to phase separation morphologies of blends

in the spinodal regime is observed [3]. Studies involving nanofillers such as C₆₀, dendrimers, and polymeric NPs have also demonstrated that the formation of an NP-rich fractal layer by direct imaging at the substrate–polymer interface pins the growth of the dewetting front in homopolymer thin films [4–10]. Recent studies also show that the exposure of low M_w (~ 2000 g/mol) homopolymer PS–C₆₀ blend films to UV ~ 3 h or ambient light ~ 24 h in the presence of oxygen can suppress dewetting. In the absence of light, the addition of C₆₀ led only to the retardation of dewetting and observable clustering of nanoparticles. [11]

We have recently demonstrated that a non-trivial coupling of polymer–polymer and polymer–NP phase separation thermodynamics in conjunction with kinetics of NP partitioning greatly affect the stabilization effects of NPs in the case of polymer blend thin film systems [12,13]. Preferential partitioning of the NPs to the polymer–polymer versus the polymer–substrate interface dominates at low ($\sim 1-4$) mass% nanofiller concentrations leading to macroscopic blend film dewetting, contrary to counterpart homopolymer thin films that are completely stabilized at similar NP concentrations. Increasing the NP concentration further to >5 mass% saturates the polymer–polymer interface and a polymer–substrate partitioning effect is observed that eventually leads to stable hybrid blend films accompanied by the development of tunable interconnected phase-separation morphology. However, all of the existing work on

* Corresponding author. Tel.: +1 330 972 8324.

E-mail address: alamgir@uakron.edu (A. Karim).

¹ Present address: BASF Corporation, 1609 Biddle Avenue, Wyandotte, MI 48335, United States.

² IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120, United States.

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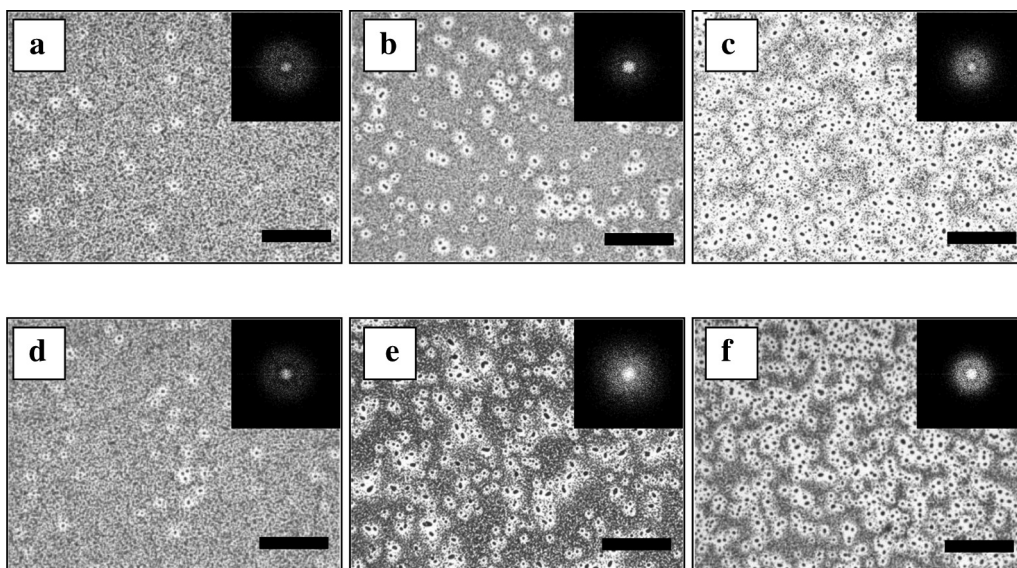


Fig. 1. Optical images of very high C_{60} concentration filled PS/PB blend thin films. (a–c): 12, 15, and 20 mass% C_{60} filled PS/PB blend thin films annealed at 95 °C respectively, (d–f): 12, 15, and 20 mass% C_{60} filled PS/PB blend thin films annealed at 130 °C. Insets show FFTs obtained using Image J data analysis software. All scale bars are 50 μm .

nanofilled polymer thin film systems involve low to medium concentration of nanofillers (<10% by mass), despite the fact that various real-life applications such as organic photovoltaics, bio-scaffolds for drug delivery, and functional coatings entail the use of relatively high concentrations of nanofillers [14–19].

In this article, we report the effects of C_{60} NPs on polystyrene (PS)/polybutadiene (PB) blend thin film stability and phase separation morphology in the high NP concentration limit (>10% by mass). Deep in the two-phase region of blend miscibility, when the mixture is away from the critical point, microscopic particle heterogeneities can induce wetting phase separation dynamics, and target pattern morphology can evolve under these conditions provided the film does not dewet the substrate. In our current work, we demonstrate a direct manifestation on phase separation morphology and thin film stability of the effects of coupling of apparent spinodal clustering of NPs with accessible spinodal phase separation of a polymer blend thin film. For our relatively low M_w polymer blend system, we are apparently on the phase boundary for C_{60} miscibility with the polymer blend system. In this ternary system, not only does an interplay between the NP–substrate interactions and NP partitioning to the polymer–polymer interface play a significant role but also the phase separation between NP spinodal clusters and the polymer blend, all of which affect phase separation dynamics and thin film stability.

2. Experimental

Polystyrene (PS), average relative molecular mass $M_w = 3000$ g/mol and a polydispersity index of 1.09 and polybutadiene (PB), $M_w = 2400$ g/mol and a polydispersity index of 1.05 from Polymer Source Inc. [20] were used for our experiments. The molecular masses were chosen so as to be similar to the ones used in a previous homopolymer–NP study [4]. Laboratory grade toluene was used as the solvent for the polymers and was purchased from BDH chemicals [20]. 1:1 PS:PB blend solutions were made by dissolving the PS and PB in common solvent toluene, such that the total polymer concentration in the solvent was 3% by mass, and the solutions were then stirred overnight. Both homopolymer and blend solutions were filtered thoroughly using a 0.2 μm PTFE filter. C_{60} NPs of purity >99%, from Sigma Aldrich Chemical Co. [20], were

dispersed in toluene, accompanied by ultra sonication, before addition to the blend solution. The nanoparticle solutions were handled inside a nitrogen purged glove bag. A series of NP-filled blend solutions consisting of C_{60} concentrations varying from 7.5 to 20 mass% relative to total polymer blend weight were prepared by dissolving the C_{60} –toluene mixture with the blend solutions. Blend thin films of thicknesses 110 ± 2 nm were prepared by spin coating on nitrogen blow dried and UVO cleaned p-type Si (100) wafers from Silicon Quest International [20]. At the 1:1 PS:PB ratio, the pure blend has an upper critical solution temperature (UCST) behavior with a critical temperature, $T_c = 110$ °C. The films were annealed at 90 °C, which is in the blend 2-phase region, and at 130 °C which is in the blend 1-phase region, for 24 h under vacuum. The annealed nanoparticle-filled blend films were characterized using an Olympus BX41 optical microscope, and a DI–Veeco Nanoscope V atomic force microscope (AFM) [20]. Further, a Zeiss confocal laser fluorescence microscope [19] was used in order to map out the z-stacking distribution of C_{60} in the samples. Image J

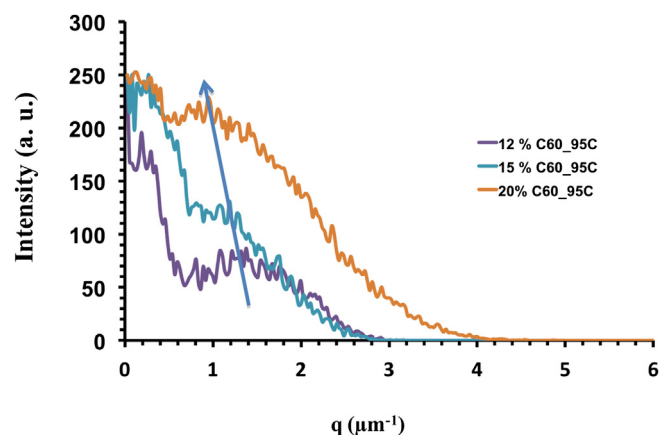


Fig. 2. Dominant length scales obtained from radial average of FFTs of optical images with different nanofiller loading, for the nanofilled blend films annealed at 95 °C (corresponds to pure blend's 2-phase region). Arrow shows how the spinodal clustering peak position q^* increases in amplitude and decreases to lower q^* with increasing nanofiller concentration.

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