Substrate dependence of morphology in thin film polymer blends of polystyrene and poly(methyl methacrylate)

DA Winesett, 1* H Ade, 1 J Sokolov, 2 M Rafailovich 2 and S Zhu 2

1 Department of Physics, North Carolina State University, Raleigh, NC 27695-8202, USA
2 Department of Materials Science and Engineering, SUNY at Stony Brook, Stony Brook, NY 11794, USA

Abstract: We studied the effects of different substrates on the development of the morphologies in thin film polymer blends in as-spun and annealed films. We have utilized thin films of blends of polystyrene and poly(methyl methacrylate) spun cast on Si, Au and Co surfaces, and produced quantitative composition maps with near edge X-ray absorption fine structure (NEXAFS) microscopy as a function of annealing time. We observed a marked dependence of the morphologies and the qualitative dynamics on the surface composition.

© 2000 Society of Chemical Industry

Keywords: PS; PMMA; homopolymer; blends; phase segregation; thin film; NEXAFS microscopy; surface

INTRODUCTION

The study of phase separation in thin films of binary mixtures is commercially important for the effective production of various coatings and films, including dielectric layers, photographic materials and paint systems. While films of polymer blends often exhibit more desirable characteristics than individual homopolymers, most blend components are also highly incompatible with each other and will demix and phase-separate. The degree of separation in blends will greatly affect the resulting morphology, which can have adverse affects on the properties of the resulting film. Conversely, a phase-separated film could exhibit more desirable characteristics, and being able to tailor the resulting morphology during preparation could prove beneficial. Therefore, understanding the variables that affect demixing morphology, and to what degree the kinetics and dynamics are influenced, are issues of considerable commercial interest. From a basic science perspective, systematic investigations of variables affecting these processes are important, because a full understanding of blend separation processes such as nucleation and growth, spinodal decomposition and Ostwald ripening are still lacking for polymer thin films.

Some details about the phase-separation process in polymers are difficult to study with conventional characterization techniques due to the inability of many of these methods to chemically differentiate materials with good spatial resolution, without damage, staining or preferential solvent washing. A characterization technique advantageous to the study of polymer films is near edge X-ray absorption fine structure (NEXAFS) microscopy in a scanning transmission X-ray microscope (STXM). 1-3 NEXAFS microscopy can be used to quantify the sample composition 4 at relatively low damage, 5 and with a spatial resolution of about 50nm. 3 Our studies complement the work of Walheim et al. 6 who primarily studied the morphology formation of the initial spin-casting process of PS-PMMA blends from three different solvents onto Si, SiOx and Au surfaces with atomic force microscopy (AFM). Walheim et al 6 also studied the annealing behaviour on Au and SiOx surfaces, but only with AFM in topography mode. We explore an additional surface, cobalt, and study the annealing behaviour on all three surfaces with direct quantitative composition maps, ie of the as-prepared films without resorting to differential dissolution of one phase.

EXPERIMENTAL

We have examined films composed of a 50/50 wt% blend of monodisperse 90000(Mw/Mn=1.05) polystyrene (PS) and 27000(Mw/Mn=1.05) poly(methyl methacrylate) (PMMA) which were purchased from Polymer Laboratories. Films were solution cast from toluene onto silicon, gold and cobalt substrates to thicknesses of approximately 50nm. The relative...
surface energies of the three substrates used were determined by measuring the static water contact angle of each of the surfaces and are summarized in Table 1. The films were annealed under vacuum for various times at 165°C, quenched to room temperature, transferred to TEM grids and examined with the Stony Brook STXM at beamline X1A at the National Synchrotron Light Source. A series of X-ray micrographs from the same sample area were acquired of each sample at energies coinciding with characteristic NEXAFS absorption peaks of the constituent components (see spectra in Fig 1). We assume a uniform density of 1.07g cm\(^{-3}\) for PS and 1.19g cm\(^{-3}\) for PMMA and normalize the reference spectra to the Henke pre- and post-absorption edge values to obtain a quantitative measurement of X-ray absorption of each polymer at a given energy. Knowing these absolute absorption coefficients, one can employ a singular value decomposition procedure to extract compositional thickness maps from the sample area.

**RESULTS AND DISCUSSION**

We have investigated a range of annealing sequences with different annealing times. We present data from three systems which represent qualitatively similar
regimens of the phase separation process. Figure 2 shows the results of the compositional mapping of a sequence of samples annealed on silicon oxide. Initially (Fig 2A–C), spin casting from toluene produces a phase-separated film with PMMA domains in a PS matrix. The spun-cast morphology is dependent on many factors, including polymer solubility, total film thickness, molecular weight and surface composition. The PMMA domains formed in our experiment are predominantly round with a domain size distribution peaked at diameters of about 200, 650 and 950 nm. We are uncertain about the origins of the particular size distribution. The larger domains in particular appear fuzzy, presumably due to a gradient interface layer or a three-dimensional, quasilayered structure where round droplets of PMMA form and wet the substrate, and where the edges might be overlapped by PS. After 10 h annealing at 165 °C (Fig 2D–F) the foam-like matrix has broken up and the PS is driving an agglomeration into three-dimensional droplets which in the total thickness map (Fig 2F) appear uniform and have smooth boundaries. However, the PMMA map shows a very different composition distribution. The valleys comprise small spherical PMMA domains that are beginning to fuse, wet the substrate and flatten. Outside the PS agglomerations, as quantitative STXM analysis reveals, is a pure PMMA matrix phase. Pure spherical PMMA domains are also seen within the rising PS regions. These smaller PMMA domains have become trapped, because they cannot recess into the very thin PMMA lower layer that wets the substrate due to the low diffusivity near the polymer–substrate interface. Similar observations have been made previously in 150 nm thick PS/PMMA (27 000/27 000) blend films on Si surfaces, and the trapped PMMA structures observed were the precursors of underlying PMMA spikes that were even observed in the late stages of coalescence. After 48 h (Fig 2G–I), the surfaces of the PS domains have smoothed out in order to lower the interfacial energy by minimizing the interfacial area. The smallest (about 3 μm) of these domains are nearly round, while the largest are still in the process of coalescing or breaking up. Quantitative analysis indicates PMMA is still continuous throughout the sample and wets the rims of the PS as evidenced by the halo around PS regions in Fig 2H. Underneath the PS domains, the PS–PMMA interface is still corrugated as a remnant of the PMMA domains that are ‘trapped’ inside the coalescing PS.

Figure 3 shows the results of the compositional mapping on a series of samples prepared on cobalt surfaces. The initial spun-cast morphology consists of phase separated PMMA domains within a PS continuum (Fig 3A–C) which are larger and generally better defined, ie more phase-separated, than the
domains on silicon. Quantitative analysis indicates that both the PMMA domains and PS matrix are essentially pure and span from the air surface to the substrate. Annealing for 20min (Fig 3D–F) leads to reorganization into a morphology with mixed phases that appears less distinct and that has, on average, smaller domains. There are clearly regions where a mixed or layered morphology develops (medium grey in the Figs 3D and E). After 48h (Fig G–I), the PMMA domains are pure, essentially round, relatively small, and span from the cobalt interface to the air surface. This is contrary to the morphology observed on the silicon surface where the PMMA forms the matrix, indicating that the relative polymer–substrate interfacial energy is higher for PMMA than for PS on a cobalt surface. Water contact-angle data (Table 1) indicates that cobalt is less polar than either gold or silicon, and so PMMA (which is more polar) will form domains rather than a continual matrix in order to minimize the cobalt–PMMA interfaces. Additionally, the topography image (Fig 3I) indicates a slight recession at the interface of the two phases. This effect is due to the energy preference of the air–PMMA interface compared with the PS–PMMA interface. In the cobalt system, the PMMA domains dewet on the PS matrix, while on silicon (Fig 2H) there are PS domains which are wetted by PMMA. Besides the initial reorganization seen in Fig 3E, we observe no significant dynamics on cobalt.

Figure 4 shows compositional maps from samples prepared on gold. As with the previous systems, spin casting from toluene (Fig 4A–C) produces separated PMMA regions within PS due to solubility differences of the two polymers. After 6h annealing (Fig 4D–F), PMMA domains are larger with less defined interfaces and appear to be coalescing to form larger regions. After 24h (Fig 4G–I), PMMA is thinner, has recessed to the substrate, and is partially wetting the large, jagged PS domains. The jagged two-dimensional PS–PMMA interface is due to resonance capillary waves. Similar behaviour has been predicted by Lattice Boltzmann calculations by Wagner and Yeomans for certain diffusion/viscosity ratios, and has been experimentally observed previously in 146nm thick PS/PMMA (27000/27000) thin films prepared on silicon. Similar to the silicon system (Fig 2), thicker PMMA regions have become trapped inside the PS and cannot recess into the very thin, highly viscous PMMA substrate interface layer.

Comparing the sequences on gold and silicon substrates shows that while the dynamics are slower on gold substrates, they are significantly faster than the results observed by Walheim et al. We attribute this to the presence of a continuous PMMA phase in both...
our sequences of samples facilitating the diffusion of PS throughout the film. Alternatively, this explains the behaviour of the cobalt system. The lack of a continuous PMMA matrix layer (quantitative analysis indicate PMMA domains extend from the cobalt substrate to air surface) means that PMMA coalescence can only occur by diffusion of PMMA across higher $M_w$ PS, so the film remains frozen in a metastable state.

CONCLUSIONS

We have used scanning transmission X-ray microscopy to study the development and evolution of the morphology in as-cast and annealed films of polymer blends on silicon, cobalt and gold substrates. The choice of substrate when preparing polymer film blends has significant effects on both the initial and final morphologies. The initial spun-cast morphology in all three systems is a PS continuum with raised islands of PMMA, although the lateral shapes of the PMMA regions differ. This effect is most probably due more to the solubility of the individual polymers in toluene than initial interactions with the substrates. Annealing for long times shows that the equilibrium morphology of films prepared on cobalt substrates is inverted relative to the morphology found on the gold and silicon surfaces. On cobalt, the PS is forming the continuous phase throughout. The presence of a continuous, interconnected PMMA matrix in the silicon and gold systems allows for significantly faster dynamics than for the cobalt system, in which the lack of a connected PMMA matrix completely inhibits any dynamics.

ACKNOWLEDGEMENTS

H Ade and D A Winesett are supported by NSF Young Investigator Award DMR-9458060. MH Rafailovich, J Sokolov and S Zhu are supported by NSF DMR-9732230 (MRSEC Program) and DOE-SGO2-93-ER45481. Data were acquired with the Stony Brook STXM at the NSLS developed by the group of Janos Kirz and Chris Jacobsen at SUNY Stony Brook, with support from DOE (DE-FG02-89ER60858) and NSF (DBI-9605045). The zone plates were developed by S Spector and C Jacobsen of Stony Brook and D Tennant of Lucent Technologies Bell Labs, with support from the NSF (ECS-9510499). The NSLS is supported by the Office of Basic Energy Sciences, Energy Research, Department of Energy.

REFERENCES