Surface segregation structure of polymer-grafted silica nano-particle in polymer thin films

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1. Introduction

Polymer brushes, assemblies of surface-tethered polymers on solid substrates, are useful for surface modification. The "grafting-from" synthetic procedure is suitable method to fabricate the densely grafted polymers on the material surfaces, however, it is not easy to fabricate the polymer brushes on a large surface area at once by the "grafting-from" method because of its complex procedure and inert chemical condition for surface-initiated polymerization reactions.

We propose the simple surface coating of polymer brush-immobilized nano-particle dispersed in polymer matrices to prepare the brush-like surface. Silica nano-particles (SiNP) covered with high-density polymer brushes are expected to segregate at the film surface, as follows. Theoretically, intermixing of polymer brush and the unbound (free) polymer chains in a matrix hardly occur even for chemically identical polymer brush and matrix when the graft density of the brush is high, because intermixing of high-density brush and free polymer is entropically unfavorable. Therefore, the self-consistent field theory predicted phase separation of the high-density polymer brush and matrix polymer to restrict a fine dispersion of polymer-grafted nano-particles or fillers in the bulk. In addition, free chain ends of grafted polymers tend to segregate at the near the surface due to its low free surface energy. In this proposal, we prepare the spin coat film of the mixture of deuterated PMMA (d-PMMA)- and hydrogenous PMMA (h-PMMA)-grafted SiNP (h-PMMA-*g*-SiNP) mixture to confirm whether the SiNP segregate near the film surface to form a brush-like structure at the surface or not by neutron reflectivity (NR).

2. Experiment

Surface-initiated atom transfer radical polymerization of MMA from alkylbromide- immobilized silica nano-particle (SiNP) (d = 12 nm) was carried out to fabricate PMMA with M_n = 100000 and M_w/M_n = 1.34 grafted on SiNP (PMMA-*g*-SiNP). A mixture of 2.0wt% d-PMMA (PMMA-d8, M_n = 68000, M_w/M_n = 1.12) and 0.03 ~ 0.06wt% PMMA-*g*-SiNP in toluene was spun casted on flat silicon wafer (20 × 50 × 0.5 mm^3) to form a thin PMMA film with 74 ~ 110 nm thickness, as shown in Figure 1(a). The film was annealed at 403 K for 1 h in thermal oven. NR measurements were carried out using a SOFIA reflectometer installed in BL-16 at MLF. The neutron beam irradiated the PMMA spin coat film on the Si substrate, and the reflected neutrons were collected by a 2D detector. Three incident beam angle (0.3, 0.7 and 1.6 degree) were used to obtain the reflectivity in a q range of q = 0.10 ~ 1.5 nm^{-1} within a 5% resolution. A 12 × 40 mm of beam footprint with was maintained on the sample surface by using incident slits. The MOTOFIT program was used to fit the reflectivity profiles to modeled scattering length density (SLD) layers, in which the thickness of each layer, SLD and Gaussian roughness were optimized to minimize the least-squares of the measured and calculated reflectivity curves. SLD of d-PMMA, SiO2, and Si were 6.62 × 10^{-4}, 3.47 × 10^{-4}, 2.07 × 10^{-4} nm^{-2} were used. All the NR measurements were conducted at 298 K.

3. Results

Reflectivity curve of a d-PMMA film containing h-PMMA-*g*-SiNP on silicon wafer after annealing at 403 K for 1 h represented sequential fringes attributable to thickness of the d-PMMA film (74 nm), as shown in Figure 1(b).

The fringes gradually became unclear with increasing *q*, probably due to the SiNP. The SLD profile in Figure 1(C) showed segregation of h-PMMA-*g*-SiNP near the interface between d-PMMA and Si wafer. NR measurement of the film before the annealing also revealed similar pattern. These results unfortunately indicated that the h-PMMA brush layer did not exit at the outer most surface of d-PMMA film. The segregation of h-PMMA-g-SiNP at the bottom of the d-PMMA film occurred probably due to gravity of SiNP and phase separation of h-PMMA brush and unbound free d-PMMA.

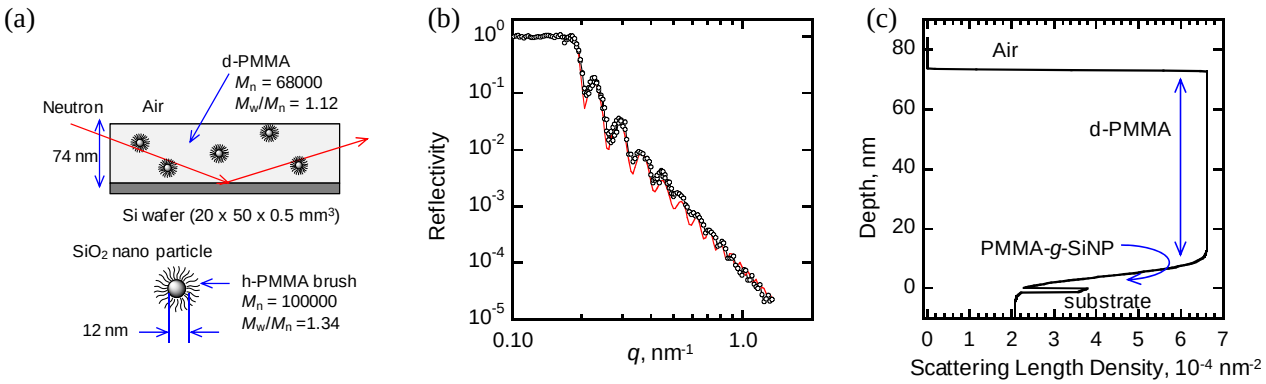

Figure 1. (a) Schematic view of d-PMMA film containing h-PMMA-*g*-SiNP on silicon wafer, (b) NR curve of the sample after annealing and the corresponding fit, and (c) SLD profile estimated by NR fitting curve.

4. Conclusions and perspective

NR measurement in this work revealed that PMMA-*g*-SiNP heterogeneously dispersed in the PMMA thin film matrix to form a concentrated region of SiNP near the interface between silicon substrate and PMMA film, probably due to the gravity. The resulting PMMA film formed an undesired structure, however, the bottom segregation of PMMA-*g*-SiNP is also interesting structure for a accumulation of polymer brush at the interface. In future work, we are going to investigate the effect of chemical structure of surface-grafted polymers, graft density, and molecular weight distribution on the aggregation structure in the polymer thin film. In addition, removal of the resulting film containing polymer-*g*-SiNP from the substrate surface will be also tried by using a sacrificial film layer on the substrate, to isolate the film with brush-like surface structure.