

Surface and Interface Structure Analysis of (Multi-functionalized Silsesquioxane/Deuterated Polystyrene) Hybrid Thin Films

N. Hosaka¹, Y. Terayama¹, M. Kobayashi², A. Takahara^{*1,2}

¹Graduate School of Engineering, ²Institute for Materials Chemistry and Engineering, Kyushu University

Polymer thin films have gained much interest because of their numerous technological applications, however, producing stable and defect-free films is problematic since the polymer thin films tend to break up and dewet from a substrate. Previously, it was shown that the addition of polyhedral oligomeric silsesquioxane (POSS) nanofiller stabilized the polystyrene (PS) thin film against dewetting [1]. POSS, which is characterized by the formula of $(\text{RSiO}_{1.5})_8$, has a nanosized cage structure with a silica core and organic groups on its surface. The dispersion state of POSS in the film seemed to be an important factor to understand the film stabilization effect [2], and the systematic study using designed nanofillers to control its dispersion state is a challenge for further development of this technique.

The present work is focused on the control of the dispersion state of POSS nanofillers in PS thin films through the introduction of the several substituents onto POSS surface. The dispersion states of the surface-modified POSS in deuterated PS (d-PS) thin films were investigated by neutron reflectivity. Figure 1 shows the depth profile models of scattering length density (b/V) of ca. 130 nm thick d-PS film and POSS/d-PS (10/90, w/w) films. POSS with phenethyl groups (PhPOSS) was homogeneously dispersed into d-PS film because of the high affinity of phenethyl groups with d-PS. The b/V of the film was decreased by the addition of PhPOSS compared with d-PS film. In contrast, POSS having seven cyclopentyl groups and a low energy fluoroalkyl group (CpPOSS-Rf) strongly segregated to the film surface and formed thin layer with low b/V . The difference of the surface energy between CpPOSS-Rf and d-

PS provides a driving force for the segregation of CpPOSS-Rf to the film surface. The formation of low b/V layer was also observed at the surface and film/substrate interface of d-PS film containing POSS with seven cyclopentyl groups and a dihydroxypropyl group (CpPOSS-2OH). CpPOSS-2OH segregated to the surface and the interface of the film because of the lower surface energy of cyclopentyl groups than that of d-PS and the affinity of the hydroxyl groups with the substrate, respectively. These results revealed that the dispersion state of POSS can be controlled by tuning the surface substituents on POSS, and expected to contribute to the design of the polymer thin film properties by the addition of nanofillers with controlled structures.

References

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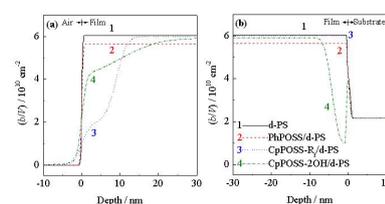


Fig. 1. Figure 1. The depth profile models of b/V of d-PS film and POSS/d-PS (10/90, w/w) films near (a) the surface and (b) the film/substrate interface.