

Growth behavior of styrene-butadiene rubber adsorption layer using reflectometry and AFM

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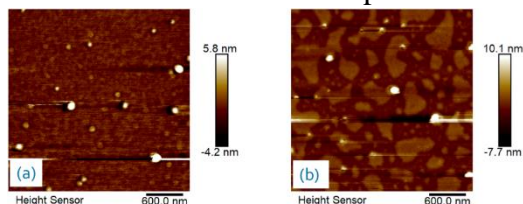
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【Introduction】 The mechanical properties of polymer composites, such as filler-filled vulcanized rubber, are generally said to be controlled by two factors: (1) enhancing the wettability of the filler surface with the matrix polymer and (2) introducing functional groups into the rubber or filler to enhance the interaction at the rubber/filler interface, thereby modifying the structure of the adsorption layer. In this study, we conducted a structural analysis of the adsorption layer of styrene-butadiene rubber (SBR) formed on a silicon substrate, focusing on the observation of the thickness and surface morphology of the adsorption layer.

【Experiment】 The SBRs were synthesized by living anionic polymerization. The weight-average molecular weights of the four types of polymers used in this study were 50,000, 102,000, 189,000, and 343,000 g/mol, respectively. The molecular weight distributions (Mw/Mn) of these polymers were 1.06, 1.06, 1.11, and 1.07, respectively. The SBRs were dissolved in toluene and spin-coated onto Si wafers. The SBR formed on a silicon substrate was annealed at 60°C for 3, 6, 24, and 48 hours, respectively, followed by leaching in toluene, and neutron reflectivity (NR) measurements were performed using BL16 SOFIA installed in the Japan Proton Accelerator Research Complex, Material and Life Science Experimental Facility. Additionally, atomic force microscopy (AFM) measurements were conducted on the same samples to observe the surface morphology.

【Result and discussion】 NR data of the samples annealed for 3 and 6 hours were fitted using a simple two-layer model, consisting of an SBR layer and a native oxide layer on the substrate. The scattering length density profiles obtained from the fitting calculations indicated that an extremely thin SBR layer of approximately 1 nm remained on the native oxide layer. This thin layer is presumed to be the inner adsorption layer of the SBR. The AFM image of the sample annealed for 3 hours also showed a uniform and flat surface structure of the inner adsorption layer (Figure 1a). For the samples annealed for 24 and 48 hours, AFM observations revealed the partial presence of a terrace structure on top of the inner adsorption layer, as shown in Figure 1b for the sample annealed for 24 hours. We speculate that the terrace structure was an energetically stable outer



adsorption layer that was not leached by toluene. Furthermore, as the annealing time increased, the area covered by the terrace structure expanded, and it was confirmed that the surface coverage varied depending on the annealing time.

Figure 1: AFM morphological images of the adsorption layers leached in toluene after annealing at 60 °C for 3(a), 24 hours(b).