MLF Experimental Report	提出日 Date of Report 2017/03/31
課題番号 Project No. 2016A0072 実験課題名 Title of experiment Aggregation Structure of Elastomer on Carbon Materials 実験責任者名 Name of principal investigator Koichiro Hori 所属 Affiliation High Energy Accelerator Research Organization	装置責任者 Name of responsible person Norifumi L. Yamada 装置名 Name of Instrument/(BL No.) BL 16 実施日 Date of Experiment 2016/12/03-2016/12/04 2017/12/08-2016/12/11

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、Figure 表添付のこと)

Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

As a material, partial deuteratied polybutadirne (PB) was used. Si wafer with 2-inch diameter were used as substrates, and carbon layer was prepared on the Si wafer. Prior to the spin-coating, three kinds of carbon layers were prepared by changing the irradiation time from 0 to 1 h, and the surface free energies evaluated by contact angle measurement using the Fowkes equation were approximately 30, 45, and 58 $mJ{\cdot}m^{-2}$, respectively. Here, we call these carbon layers carbon-30, carbon-45, and carbon-58, respectively. PB films with a thickness of approximately 55 nm were spin-coated on the prepared substrates from a toluene solution and annealed under vacuum for more than 8 h at 453 K. Then, the film was rinsed with a large amount of toluene 5 times to obtain residual layers (RLs) adhering on a carbon surface, which are model bound rubber layers (BRLs). After evaluation of neutron reflectivity (NR) measurement, deuterated PB (d-PB) was casted on the RL and dried under vacuum for 8 h at room temperature.

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。)

Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

A scattering length density (b/V) profile of the bilayer films along the direction normal to the surface was evaluated by NR measurement using a SOFIA reflectometer (BL16). Incident neutrons with a wavelength ranging from 0.25 to 0.88 nm were guided into the specimen with an incident angle of 0.3, 0.7, and 1.6° and a footprint of 40 × 30 mm^2.

Figure 1 shows NR curves for the bilayer film before and after annealing. For clarity, each data is offset by two decades. Open symbols depict experimental data and solid curves show the calculated reflectivity based on the model (b/V) profiles. Here, we focused on the (b/V) of RL, $(b/V)_{RL}$, and the interfacial roughness, σ_{int}. Table 1 summarizes the $(b/V)_{RL}$ and σ_{int} values before and after annealing. For comparison, (b/V) of the RL before adding d-PB calculated using the density are also listed in Table 1. First, $(b/V)_{RL}$ of the RL on carbon-58 after the formation of a d-PB layer was larger than that of the RL without the d-PB layer, and it increased upon annealing.

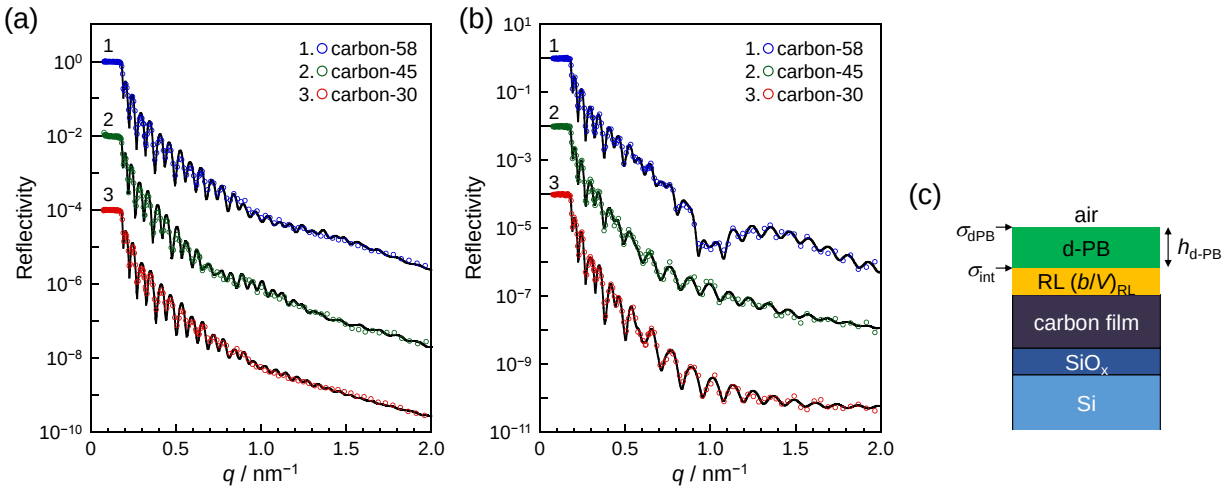

Figure 1 Neutron reflectivity curves of (RL/d-PB) bilayer on the carbon film (a) before and (b) after annealing. Solid curves show calculated reflectivities on the basis of model scattering length density profiles. (c) Schematic illustration of the model used for the bilayer.

Table 1 Scattering length density of RLs $(b/V)_{RL}$ and interfacial roughness of (RL/d-PB) interface σ_{int} before and after annealing. For comparison, $(b/V)_{RL}$ of the RL before coating of the d-PB layer estimated from the density is also listed.

	RL without d-PB layer	Before annealing		After annealing	
	$(b/V)_{RL}$ / nm^{-2}	$(b/V)_{RL}$ / nm^{-2}	σ_{int} / nm	$(b/V)_{RL}$ / nm^{-2}	σ_{int} / nm
RL(carbon-58)	4.26×10^{-5}	1.02×10^{-4}	1.3	2.28×10^{-4}	2.6
RL(carbon-45)	4.73×10^{-5}	4.73×10^{-5}	1.4	8.74×10^{-5}	2.4
RL(carbon-30)	4.97×10^{-5}	4.97×10^{-5}	0.9	4.97×10^{-5}	1.2

This indicates that a part of the d-PB chains has already penetrated into the RL during spin coating of the d-PB layer, and the intermixing of the molecules between the RL and d-PB layers are enhanced by the annealing. In contrast, no change in $(b/V)_{RL}$ was observed and only σ_{int} increased upon annealing in the case of the RL on carbon-45 and carbon-30 (the change in the NR profiles was mainly caused by the change in the roughness of the d-PB surface, $\sigma_{d\text{-}PB}$, for all the cases). Note here that σ_{int}. of carbon-45 increased to a greater extent than that of carbon-30; that is, the PB molecules in the RL on the carbon-45 were slightly more mobile than those on carbon-30. These results suggest that the mobility of the PB molecules in the RLs is strongly suppressed depending on the surface energy of the carbon films.