

# Interface analysis of deuterated and non-deuterated polyamide 66 with neutron reflection

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## 1. Introduction

Polyamide 66, namely nylon 66, is widely accepted as an engineering plastic in the field of the vehicle industry. Therefore, the component materials based on polyamide 66 are integrated in the vehicle framework. However, polyamide 66 has an disadvantage on its adhesion property and the low adhesion property leads to the trouble of the products. Additionally, the weld line formed in the molding process and the weak boundary interface of thermal fusion trigger mechanical defects of the products. The analysis of interface consisted of components with the same chemical structure in the weld lines is a challenge because of no difference between their components. The mechanical property at the adhesion interface depends on the thickness of the adhesion layers. The interfacial layer is controlled by mutual diffusion of their components. Therefore, we investigate the mutual diffusion of polyamide 66 at the interface from the view point of molecular dynamics. The polymers with the same chemical structure in their interface layers were not able to discriminate with one another in conventional method such as X-ray and microscopic measurements.

We focused on the interface between protonated and deuterated polyamide 66 in order to detect them spectroscopically with Raman scattering and neutron beam. In advance, we investigated their structure and properties. The mechanical and thermal properties of protonated and deuterated polymers are remarkably similar, whereas Raman scattering bands originated from CH<sub>2</sub> and CD<sub>2</sub> and neutron scattering length densities are significantly different. The measurements with Raman scattering and neutron beams detect the difference in their polymers. Moreover, the neutron beam possesses high material permeability. Therefore, the analysis of ever inner interfacial structure by neutron beams can be accessed non-destructively. The elucidation of their interfacial structure leads to the mechanism of the adhesion of the same polymer.

Herein, we prepared double-layers on silicon wafers with protonated and deuterated polyamide 66 (H-PA66 and D-PA66) and investigated their interface structures with time-sliced neutron reflectivity (NR) measurements. We have synthesized D-PA66 and H-PA66 and measured their thermal properties and structure. Their thermal properties and structures were corresponded with each other, while in the NR measurements of single-layered films, their thin films were distinguished.

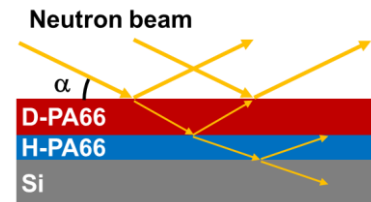


Figure 1. D-PA66/H-PA66 double layer model.

## 2. Experiment

We prepared D-PA66/H-PA66/Si samples, as shown in Figure 1. Before thermal annealing, we measured NR of their samples at room temperature. The  $q$  ranges in the NR measurements were from  $0.01 \text{ \AA}^{-1}$  to  $0.10 \text{ \AA}^{-1}$ . We analyzed and fitted the NR profiles with Motofit software.

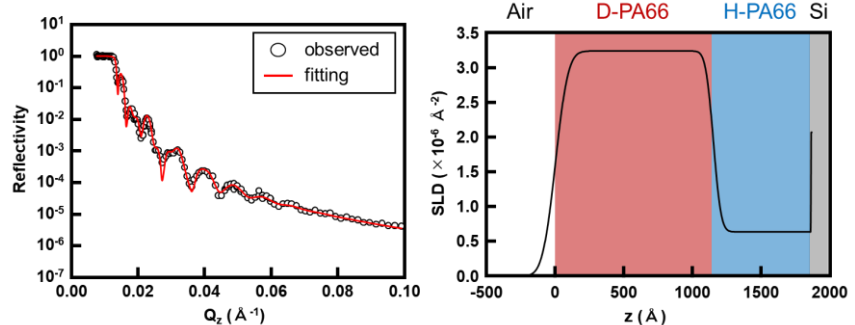


Figure 2. NR and SLD profiles of D-PA66/H-PA66 double layer at room temperature.

Next, under thermal annealing, time-sliced neutron reflective measurements were performed at 80 °C, 120 °C, 150 °C and 230 °C. The  $q$  ranges in the NR measurements were from  $0.01 \text{ \AA}^{-1}$  to  $0.06 \text{ \AA}^{-1}$ .

### 3. Results

Figure 1 shows NR profile of D-PA66/H-PA66/Si at room temperature and the fitting data. From the neutron scattering density profiles, the thickness of D-PA66 and H-PA66 were 114.9 nm and 71.0 nm, respectively. The thickness of interfacial region was 4.4 nm. The obtained thickness of films corresponded approximately to the results from AFM topological images.

The time-sliced NR profiles under annealing at various temperature are shown in Figure 3. Under annealing at less than 150 °C, the NR profiles were not changed for 8 h. In contrast, under annealing at 230 °C, the NR profiles were changed within the first hour. Therefore, we focused on the NR profiles within 30 min annealing time. The gradual changes of the NR profiles were observed.

In the laminated films with 200  $\mu\text{m}$  thickness, it was observed from the Raman scattering measurements with line scanning that the expansions of interfacial region were enhanced by annealing at 150 °C. The results were contradictory to NR measurements. The reason would be that the laminated films with 200  $\mu\text{m}$  thickness were prepared with heat-pressing under 6.0 MPa, while the double layers were annealed under non-pressure in the time-sliced NR measurements.

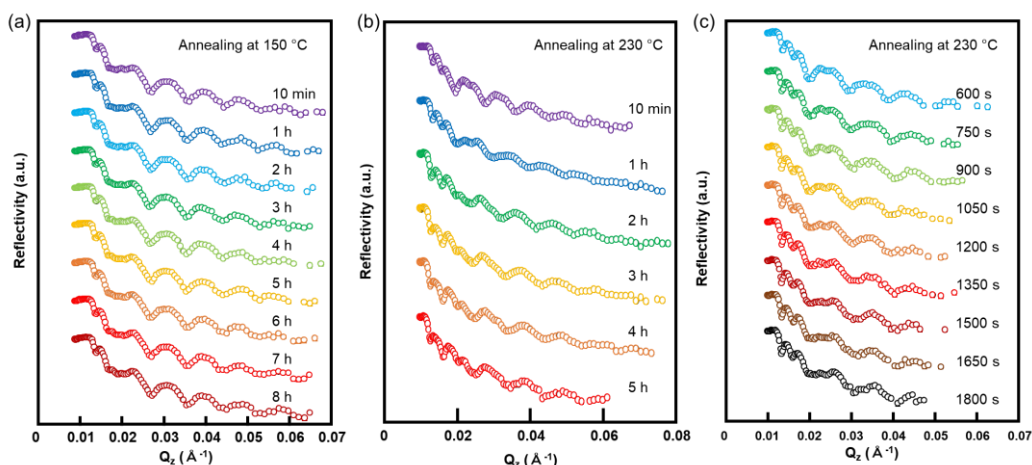


Figure 3. NR profiles of D-PA66/H-PA66 double layer at (a) 150 °C, (b) 230 °C and (c) 230 °C in the first 30 min.

### 4. Conclusion

It is proved from the obtained NR profiles that the double layers with low roughness were formed. From time-sliced NR measurements, the structure of the double layer was changed by annealing at 230 °C, not at 150 °C. Unfortunately, the results disagreed with the experiments of laminated films with 200  $\mu\text{m}$  thickness.

Therefore, we have plans to measure time-sliced NR of the double layers under thermal annealing with compression pressures. We are going to apply this proposal as 2018B term experiments.