

## Structural analysis of a poly(oxyethylene) crystal in poly(*d,l*-lactide) / poly(oxyethylene) blends and its melting behavior

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### 1 Introduction

Poly(lactic acid) (PLA) plays an important role in the family of biodegradable aliphatic polyester due to its various fields of application especially in the drug delivery system or for biomedical products. It has been known that blending of polymers is a cost effective method to improve poor properties of PLA. Since poly(oxyethylene) (PEG) is miscible with PLA in the amorphous phase, it has been incorporated in our research. To investigate the higher-order crystalline structures in blends, we prefer an amorphous/crystalline blends system. Thus, we use non-crystalline PLA (DLPLA) for blending as in our previous work<sup>1</sup>. In this study, we report comprehensive melting behavior of the PEG crystallites in DLPLA/PEG blends with various compositions in the heating process.

### 2 Experiment

Poly(*d,l*-lactic acid) (DLPLA) ( $M_w = 75,000 \sim 120,000$ ,  $T_g = 44^\circ\text{C}$ ) and PEG ( $M_w = 20,000$ ,  $T_m = 65.5^\circ\text{C}$ ) were used in this study. Blend samples were prepared by the solution-cast in a flat Petri dish from a dichloromethane solution having ca. 5 wt% polymer concentration. The blend is referred to as DLx, where x represents the weight percentage of DLPLA in the blend. The SAXS measurements were carried out at BL-6A and BL-9C beamlines of the Photon Factory, KEK, Tsukuba, Japan, which provide the high brilliant synchrotron X-rays.

### 3 Results and Discussion

We found that the lamellar stacking was much more regular for the blends, especially in case of DLPLA/PEG = 20/80 wt% (DL20) than for the PEG 100% sample as shown in Fig. 1. Furthermore, particle scattering was observed at just only  $1^\circ\text{C}$  below  $T_m$  of PEG for the PEG 100% sample and other blend samples (except for DL80). By conducting model calculation<sup>2</sup> of the SAXS profiles near  $T_m$ , we could obtain thickness of lamellae (distribution function) as shown in Fig. 2 for all samples (PEG 100%, DL5, DL10, DL20 and DL50). In addition, it was found that the repeating period of crystalline lamellae became longer and longer as the sample temperature approaches to  $T_m$ . To explain this intriguing melting behavior, it is noted that the thinner lamellae were already melted away and the thickest ones only remain at that high temperature, which was confirmed in Fig. 2 by observing very sharp lamella-thickness distribution around 33.5 nm for all of the blend samples (except for DL80).

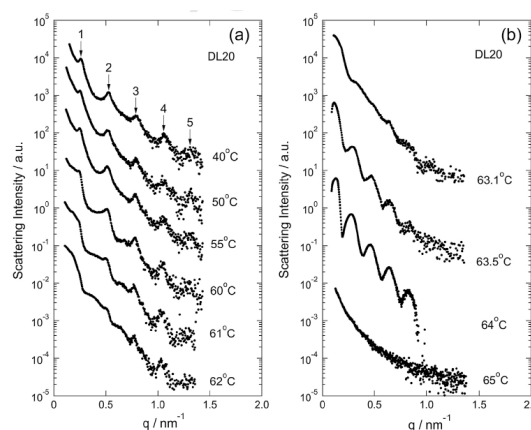


Fig. 1: 1d-SAXS profiles measured during the heating process (a) from 40 to  $62^\circ\text{C}$ , and (b) from  $63.1$  to  $65^\circ\text{C}$  for DL20 blend sample.

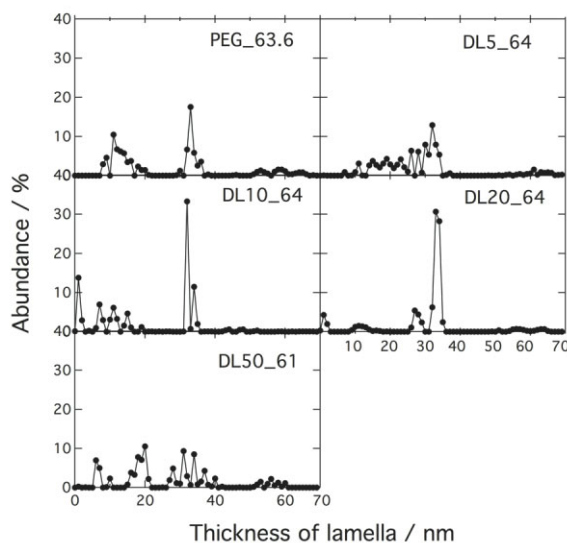


Fig. 2: Change in the abundance of lamellar thickness for blend samples.

### References

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