Effects of blending poly(D,L-lactide) with poly(ethylene glycol) on the higher-order crystalline structures of poly(ethylene glycol) as revealed by small-angle X-ray scattering

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Abstract. Effects of blending poly(lactic acid) (PLA) with poly(ethylene glycol) (PEG) on higher-order crystalline structures of PEG were examined using small-angle X-ray scattering (SAXS). For this purpose, the fact that two polymers are both crystalline makes situation much complicated. To simplify, non-crystalline PLA is suitable. Thus, we used poly(D,L-lactic acid) (DLPLA), which is random copolymer comprising D- and L-lactic acid moieties. Multiple scattering peaks arising from the regular crystalline lamellar structure were observed for the PEG homopolymer and the blends. Surprisingly, the structure is much more regular for the blend DLPLA/PEG at composition of 20/80 wt.% than for the PEG homopolymer. Also for this blend sample as well as for a PEG homopolymer, very peculiar SAXS profiles were observed just below T_m of PEG. This is found to be a particle scattering of plate-like objects, which has never been reported for polymer blends or crystalline polymers. Furthermore, it was found that there was strong hysteresis of the higher-order structure formation.

1. Introduction
Poly(lactic acid) (PLA) is at present the most promising and interesting biodegradable polymers in the family of aliphatic polyester. Polylactides have a chiral carbon in the lactic acid unit, giving rise to two stereoisomers, poly-L-lactide (PLLA) and poly-D-lactide (PDLA). Both are highly crystalline in contrast to racemic poly-DL-lactide (DLPLA) which is amorphous consisting of both D- and L-lactic acid 1.

Because of rather poor properties such as poor thermal stability 2,3 and highly sensitive to heat 4,4, poor long-term durability 2,5 and lower impact strength 5,6 several approaches can be used to improve the properties of PLA 3,7. Blending of polymers is a relatively simple and more cost-effective method in comparison with other methods.

Until now, not only block copolymers of PLA and poly(ethylene glycol) (PEG) have been developed 8,9 but also miscibility and crystallization behaviors of PEG/PLLA blends have been paid much attention in many papers. It was reported that crystallization behavior of PLLA could be
influenced in the existence of PEG\textsuperscript{10-13}. In summary, PEG/PLA blends range from miscible to partially miscible, depending on composition\textsuperscript{14-17}.

In this study, PEG was used to make the blend with non-crystalline PLA (DLPLA) for promising improvement of the mechanical properties without lowering biodegradability, because PEG is also biodegradable. We examine effects of blending DLPLA with PEG on the higher-order crystalline structures of PEG by applying small-angle X-ray scattering (SAXS) measurements using high brilliant synchrotron radiation to detect nanostructures in the blends.

2. Experimental

The DLPLA sample was purchased from Sigma-Aldrich Co. and its weight-average molecular weight is in the range of 75,000 - 120,000. PEG with average molecular weight 20,000 was purchased from Wako Pure Chemical Industries, Ltd. (T\textsubscript{m} = 65\degree C measured by DSC). The use of the non-crystalline DLPLA sample enables us to examine the effect of blending on the higher-order crystalline structures of PEG, easier than for the case of the crystalline/crystalline blends.

All the blend samples were prepared by solution-casting method. Given amounts of DLPLA and PEG were dissolved in dichloromethane yielding ca. 5 wt% solution. The solution was poured into a Petri dish. A film was obtained after complete evaporation of dichloromethane under ambient condition at room temperature.

The SAXS and WAXS (Wide-angle X-ray scattering) measurements using the high brilliant synchrotron X-rays were carried out at BL-9C with the wavelength of 1.5\AA\ and BL-10C beamlines with wavelength of 1.488\AA\ of the Photon Factory in the High Energy Accelerator Research Organization, Tsukuba, Japan. The imaging plate (250 x 250 mm\textsuperscript{2}), of which actual pixel size is 100 x 100 \mu m\textsuperscript{2}, was used as a two-dimensional (2d) detector. The typical exposure time was in the range 30-100s for SAXS and 10-30s for WAXS, respectively. BAS2000 (Fuji Photo Film Co., Ltd.) was used for development of exposed 2d images. The 2d-SAXS and 2d-WAXS patterns were further converted to one-dimensional profiles by conducting circular average and sector average.

3. Results and Discussion

Figure 1 shows the change in the one-dimensional SAXS (1d-SAXS) profiles measured at room temperature (around 25\degree C) for the PEG homopolymer (DL0) and various blend samples with different compositions. These profiles were obtained from two-dimensional SAXS (2d-SAXS) patterns by conducting the circular average, where \( q \) denotes the magnitude of the scattering vector as defined by \( q = \left( \frac{4\pi}{\lambda} \right) \sin \left( \frac{\theta}{2} \right) \) with \( \lambda \) and \( \theta \) being the wavelength of X-ray and the scattering angle, respectively.

For the PEG homopolymer (DL0) sample, multiple scattering peaks up to the fourth-order with the relative angular position of 1:2:3:4 are discernible. This suggests crystalline lamellae of PEG are regularly\textsuperscript{18}. From the position \( q^* \) of the first-order peak (\( q^* = 0.264 \text{ nm}^{-1} \)), the long period of the PEG crystalline lamellae was evaluated as 23.8 nm through the Bragg’s equation \( d = \frac{2\pi}{q^*} \).

As for the blends, it is surprisingly found that the regularity became much better by blending 20 wt% of DLPLA (DL20), which can be concluded from the 1d-SAXS profile for the DL20 sample, exhibiting much sharper peaks than for the PEG homopolymer. Note here

![Figure 1. 1d-SAXS profiles for the PEG homopolymer (DL0) and various DLPLA/PEG blend samples (DL20, DL50, DL80) with different composition.](image-url)
that the peak positions do not change, indicating no effect of blending on the lamellar repeating period. For the blending 50wt% of DLPLA (DL50), the peaks became broader as compared to the case of the homopolymer without changing the peak positions, as well. This means that the regularity of the lamellar stacking is spoiled by blending 50wt% of DLPLA without changing the repeating period. By further blending (80wt% of DLPLA; DL80), the 1d-SAXS profile is completely changed. One can find a broad peak at $q^* = 0.376 \text{ nm}^{-1}$, which gives the lamellar repeating period of 16.7 nm, 29.8% reduction of the period as compared to the homopolymer. The regularity of the lamellar repeating becomes very worse because the crystallinity of PEG is lowered by the large amount of amorphous DLPLA. The change in the repeating period with the blend composition is shown in Figure 2.

We are not sure why the 20wt% blending of DLPLA makes the PEG lamellar stacking much regular. One possible explanation may be due to the smooth interphase between crystalline and amorphous region for the blend than for the homopolymer because of more the regular chain folding. Also the change in the lamellar repeating period with the blend composition should be explained in the light of the miscibility between DLPLA and PEG in the amorphous phase. For this purpose, we further conducted the temperature dependence of the SAXS and WAXS measurements for the DL20 sample. The result is shown in Figures 3 and 4.

![Figure 2. Change in lamellar repeating period with blended DLPLA content.](image2)

![Figure 3. Change in 1d-SAXS profile with temperature (heating process) for the DL20 sample.](image3)

![Figure 4. Change in 1d-WAXS profile with temperature (heating process) for the DL20 sample.](image4)
Though the SAXS and WAXS measurements were not conducted simultaneously, they can give supplementary information. Many higher-order SAXS peaks were observed for 40 ~ 55°C due to the regular stacking of the crystalline. One can see the critical changes in the SAXS profiles at 64°C and 65°C. Since 65°C is above the melting temperature of PEG, crystalline lamellae are subjected to melting. Therefore, no peak was observed both in the SAXS and the WAXS profiles (except for the amorphous peak in the WAXS profile). It is noticeable that the higher-order structure at only 1°C below (at 64°C) in the blend gives such a peculiar 1d-SAXS profile, which is completely different from the one measured at room temperature up to 60°C in the heating process. The scattering comprises contributions from inter- and intra-particle interferences and those are referred to as lattice and particle scattering, respectively. This shape of the profile reminds us a scattering function for an isolated particle, we calculated model scattering function of an isolated lamellar particle.

From the best fitting between model calculation and the experimental curve, the thickness of the lamellar particle (L) was determined to be 36.5 nm. However, there is crucial deviation around q = 0.1 nm⁻¹. Especially, the model calculation cannot explain the peak at q = 0.13 nm⁻¹ in the experimental profile. If it would be the first-order lattice peak, which gives the repeating period of 48.7 nm, the crystallinity estimated by L/D (L: lamellar thickness (36.5 nm) and D: lamellar repeating distance (48.7 nm)) would be 75%. This is ridiculously large at temperature just 1°C below Tm. As a matter of fact, by conducting peak decomposition of the WAXS profile measured at 64°C, we evaluated the crystallinity 12%. Although it seems that the model with L = 36.5 nm and D = 48.7 nm may be non-realistic, there would be still a possible explanation if we consider that small grains, which contain a stack of the small number of the crystalline lamellae with thickness of 36.5 nm and the spacing of 48.7 nm, are sparsely dispersed in the matrix of completely amorphous phase.

In case that the peak around q = 0.13 nm⁻¹ may not be the first-order lattice peak, we should improve modeling of the form factor. It should be noted that the model calculation we employed assumes the infinitesimal extent (width) of the plate-like particle. We should do calculation again with a finite size of the plate.

Figure 5 shows 2d-SAXS patterns for the through and edge view geometries of the as-cast sample (DL20). The edge view shows diffraction arcs (first- and second- order lattice peaks) with intensity...
accumulation in the equatorial direction, which is perpendicular to the normal of the as-cast film. This fact suggests that the crystalline lamellae are oriented more or less perpendicular to the surface of the as-cast film.

Why was such preferential perpendicular orientation spontaneously obtained? To explain this interesting phenomenon, temperature gradient due to the endothermic effect by the solvent evaporation during the solution cast may be a clue. To examine whether the PEG crystalline lamellae can be oriented by the temperature gradient, we have conducted separate experiments of thermal annealing of the PEG homopolymer under a horizontal temperature gradient and found that the crystalline lamellae were oriented parallel to the temperature gradient direction. Therefore, this result can explain the spontaneous perpendicular orientation of the PEG lamellae in the as-cast film of the DLPLA/PEG blend sample due to the vertical temperature gradient induced by the solvent evaporation. Thus, further controls of the perpendicular orientation in the as-cast film promise to provide a material with special anisotropic properties by the simplest technique just like a solution casting.

To reveal higher-order structure formation from the melt upon cooling, we conducted SAXS measurements upon cooling from 65°C. As shown in Fig. 6(a) neither particle nor lattice scattering appeared upon cooling from 65°C. This result indicates that once the sample was melted away, the regular higher-order structure was not reformed. Here, it is noted that we confirmed crystallization by WAXS as shown in Fig. 6(b). Therefore, it is suggested that the regular crystalline lamellae (namely, the regular folding of the PEG chains) cannot be formed spontaneously although the crystallization of the PEG chains takes place. For further understanding of this strong hysteresis of the structural reformation, the SAXS measurement was conducted upon cooling from 64°C, as shown in Fig. 6(c). Note that in this case we are intended to examine whether the regular lamellar stacking can take place or not upon cooling from 64°C where we still observed the particle scattering as shown in Fig. 3. Since no lattice peak appeared, it is concluded that the lamellar stacking did not take place spontaneously, even in the case of cooling from the state where the regular isolated lamellae exist. Overall, we came conclusion that not only the chain folding but also the stacking of the isolated lamellae cannot take place spontaneously upon cooling. Taking into account of the fact that the lattice peaks were observed for the as-cast sample (Fig.1 & 3), the solution casting can be considered as a good technique for obtaining such regular higher-order crystalline structure. Finally, we should note that although the position of these peaks are slightly higher as compared to the case of the as-cast sample (Fig. 3), the lattice peaks were observed (Fig. 6a) after 8 days elapsed after the crystallization at room temperature from the melt (65°C). Therefore, this result reminds that the formation of the regular higher-order crystalline structure takes comparatively long time.
4. Conclusion

In this study, blends samples of non-crystalline DLPLA and PEG were subjected to structural analyses to examine effects of blending PLA (bio-based materials) with PEG on the higher-order crystalline structures of PEG. The structure is much more regular for blend (DLPLA/PEG = 20/80)
than for the PEG homopolymer by observing many higher-order lattice peaks in the SAXS profile. Furthermore, for DLPLA/PEG = 20/80 blend sample, very peculiar SAXS profiles were observed just 1°C below T_m of PEG. This is found to be a plate-like particle scattering, which has never been reported for crystalline polymers. In addition, it was found that there was strong hysteresis of the higher-order structure formation. Once the sample was melted away, the regular higher-order structure was not reformed. However, confirmed crystallization by WAXS suggests that the regular folding of the PEG chains cannot be formed spontaneously although the crystallization of the PEG chains takes place. In case of cooling from the state where the regular isolated lamellae exist, no lattice peak appeared. Therefore, not only the chain folding but also the stacking of the isolated lamellae cannot take place spontaneously upon cooling. Finally, the lattice (SAXS) peaks were observed after more than 1 day elapsed after the crystallization at room temperature from the melt (65°C) reminds that the formation of the regular higher-order crystalline structure takes comparatively long time.

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