

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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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. Because of rather poor properties such as poor thermal stability and highly sensitive to heat, poor long-term durability and lower impact strength several approaches can be used to improve the properties of PLA. 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 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. In summary, PEG/PLA blends range from miscible to partially miscible, depending on composition.

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.

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 Å and BL-10C beamlines with wavelength of 1.488 Å of the Photon Factory in the High Energy Accelerator Research Organization, Tsukuba, Japan. The imaging plate (250 x 250 mm²), of which actual pixel size is 100 x 100 μm², 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.

In conclusion, we have found the following interesting results. 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 (650C) reminds that the formation of the regular higher-order crystalline structure takes comparatively long time.

Finally, we like to report on the perpendicular spontaneous orientation. Figure 1 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

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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.

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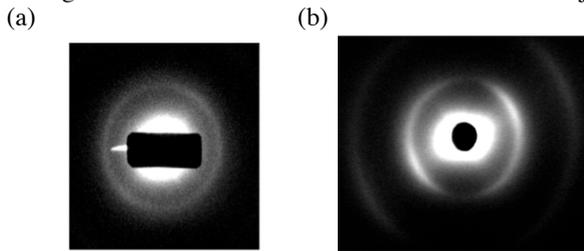


Fig. 1 2d-SAXS patterns of through view (a) and edge view (b) for the as-cast sample (DL20) at room temperature.