Research Article

Structural Investigation of Poly(lactic acid) Cast Film by Using Synchrotron X-ray Scattering Technique

Suttinun Phongtamrug* and Phatcharin Phakpharin
Department of Industrial Chemistry, Faculty of Applied Science, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand
Integrated Nanoscience Research Center, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand

Siriwat Soontaranon and Supagorn Rugmai
Synchrotron Light Research Institute, Nakhon Ratchasima, Thailand

* Corresponding author. E-mail: suttinun.p@sci.kmutnb.ac.th DOI: 10.14416/j.ijast.2018.03.002
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Abstract
Microstructure of polymer relates obviously to the materials' properties. Understanding the orientation and arrangement of the structure guides how to obtain the desirable properties of the final product. This work investigated the preliminary structure of poly(lactic acid) (PLA) cast film by using synchrotron X-ray scattering technique. The PLA was compounded with an epoxidized soybean oil (ESO) and a microcrystalline cellulose (MCC) as a plasticizer and a nucleating agent, respectively. The film products were prepared by using a chill-roll cast film extruder. Orientation and crystal structure of the PLA cast films without and with additives were characterized by two-dimensional small angle X-ray scattering (2D-SAXS) and wide angle X-ray diffraction (2D-WAXD) techniques. Moreover, investigation on post-processing, i.e. stretching at room temperature, was carried out by using a homemade stretcher. Varieties of chain arrangement due to the additives and stretching were exhibited.

Keywords: X-ray scattering, Poly(lactic acid), Cast film, Stretching

1 Introduction

Structural arrangement and molecular orientation of polymer relate explicitly to the properties of materials. Many attempts have been carried out to clarify the microstructure of the polymer in order to decide the desirable properties of the final product.

Poly(lactic acid) (PLA) has been known as one of the promising biodegradable polymer which has been commercialized due to its particular properties such as transparency, high tensile strength, and easy processability. However, its disadvantages are slow crystallization rate and brittleness which impact on long-time post-processing and mechanical properties of the final product. To improve PLA properties, compounding PLA with various types of additives have been technically used in commercial markets [1]–[3].

A plasticizer is one of the most important additives to provide the necessary workability to polymer and assist flowability of polymer during processing. A modified oil is one example that has been widely used for many commercial products such as addition of epoxidized soybean oil (ESO)

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into poly(vinyl chloride) [4]. Recently, it also have been applied in PLA for biodegradable plastic product [5]–[7]. On the other hand, to increase crystallization rate and improve mechanical strength of the product, cellulose has been chosen as a nucleating agent in the study because of many attractive points, e.g. biodegradability, biocompatibility, and inexpensiveness. Many researchers showed that the cellulose increases crystallization rate and improves mechanical strength of the polymer [8]–[10]. Moreover, combination of various kinds of additives somehow promotes the mechanical properties as seen in the example of toughness improvement by using microcrystalline cellulose (MCC) and ESO [11]. Up to now, there are many reports on enhancement of thermal and mechanical properties of the PLA-based bioplastics. However, to the best of our knowledge, there has been no report on microstructural investigation of the PLA cast film prepared by a chill-roll cast-film extruder.

In this work, the microstructure in the PLA cast film was investigated by synchrotron X-ray scattering technique. The effect of adding plasticizer and nucleating agent, i.e. epoxidized soybean oil and microcrystalline cellulose, respectively, have been studied. Furthermore, effect of post-processing such as stretching have been carried out. This will initiate an idea of controlling processing condition to acquire the desired properties.

2 Materials and Methods

2.1 *Materials*

Poly(lactic acid) (PLA) with the trade name Ingeo^{TM} 2003D was obtained from NatureWorks LLC, USA. Epoxidized soybean oil (ESO) with an epoxy value ~6% and iodine value < 5% was bought from Chemmin Corporation Ltd., Thailand. Microcrystalline cellulose (MCC) was a product of Sigma-Aldrich Co. LLC, Singapore.

2.2 *Preparation of cast films*

PLA pellets were first dried at 60°C overnight. ESO and MCC were mixed with PLA and introduced to a twin-screw co-rotating extruder (Prism TSE 16 TC, Thermo Electron Corporation, USA) with length to diameter ratio (L/D) of 25 operating at 160–170°C and 10 rpm. The mixing ratios of all components were shown in Table 1. The extrudate was cut into a pellet with a pelletizer. The film samples were prepared by using a chill-roll cast-film extruder with a T-shape die (LE 25-30/C and LCR-300, Labtech Engineering, Thailand) operating at 160–220°C and 20–25 rpm. The film samples obtained were annealed at 110°C for 30 min.

Table 1: List of the PLA compounded film

Formula	PLA	ESO	MCC
PLA	100	-	-
PLA95/ESO5	95	5	-
PLA95/MCC5	95	-	5
PLA95/ESO2.5/MCC2.5	95	2.5	2.5
PLA90/ESO5/MCC5	90	5	5
PLA85/ESO7.5/MCC7.5	85	7.5	7.5

2.3 *SAXS and WAXD measurements*

Lamellar and crystal structures of the sample films were studied by using synchrotron radiation (λ = 0.1378 Å) at synchrotron light research institute, Thailand. The film sample was hold in vertical position along a machine direction. Small angle X-ray scattering (SAXS) patterns were taken by using a CCD detector with a 4000 mm camera length. Wide angle X-ray diffraction (WAXD) patterns were taken by using a CCD detector. Styrene-ethylene/butadiene-styrene copolymer (SEBS) and 4-bromobenzoic acid were used as standard for SAXS and WAXD sample-to-detector distance calibration, respectively. The patterns obtained were subtracted by air as background. All data was analyzed by using self-developed program, SAXSIT software.

Long period (L) was calculated by using Bragg's law as indicated in the Equation (1) below,

$$L = \lambda/2 \sin \theta \quad (1)$$

where λ is a radiation wavelength, and θ is a diffraction angle.

The film samples were stretched in a machine direction by using a homemade stretcher. The stretched length was measured by using ImDistMeas software.

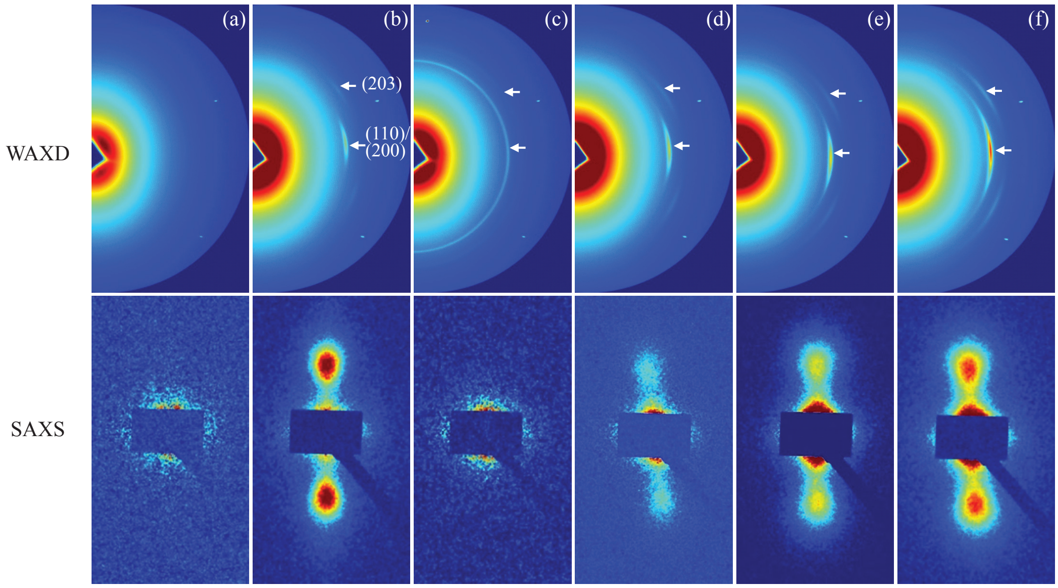

Figure 1: WAXD and SAXS patterns of the PLA compounded cast films ((a) PLA, (b) PLA95/ESO5, (c) PLA95/MCC5, (d) PLA95/ESO2.5/MCC2.5, (e) PLA90/ESO5/MCC5, and (f) PLA85/ESO7.5/MCC7.5) taken at room temperature.

3 Results and Discussions

3.1 *Structure of the PLA film at room temperature*

Microstructure of the annealed cast films was investigated by using synchrotron radiation. The WAXD and SAXS patterns of the PLA films taken at room temperature are shown in Figure 1.

Crystal structure of PLA mainly shows the WAXD pattern of a (110)/(200) reflection and a (203) reflection [8]. However, for the PLA cast film obtained, unclear reflection was observed in the WAXD pattern and blurred pattern was found in SAXS pattern. This showed that the structure in the PLA cast film might consist of mainly amorphous structure and no lamellar orientation occurred.

3.2 *Structural study of the compounded films*

Addition of ESO in the PLA film gave a sharp reflection in the equatorial line and the slight streaks which is corresponding to the (110)/(200) reflection and (203) reflection, respectively [Figure 1(b)]. For SAXS pattern, a two-point pattern was observed and long period was about 25 nm. This showed that ESO somehow assists crystallization and lamellar orientation in the PLA film. Moreover, the crystal and lamellar structure of PLA aligned in the machine direction. In the case of adding MCC, a sharp reflection appeared in the WAXD pattern but no clear reflection was observed in the SAXS pattern [Figure 1(c)]. This implied some PLA crystal structure nucleated and randomly dispersed in the film sample.

Effect of both additives were also considered. The ESO and MCC were compounded into the PLA film. The WAXD and SAXS patterns of all PLA/ESO/MCC films [Figure 1(d)–(f)] were quite similar to that of the PLA/ESO film. However, the clearer reflection were obtained in the case of PLA/ESO/MCC. When the amount of both additives was increased, the WAXD reflection became broader deviating from the machine direction while the SAXS patterns showed more obvious two-point pattern. This showed us that ESO and MCC induced crystal nucleation and lamellar structure in the film sample. Increasing of MCC caused crystal structure of PLA aligned in a disordered position. However, increase in amount of ESO assisted lamellar orientation and maintained lamellar structure as well as a long period.

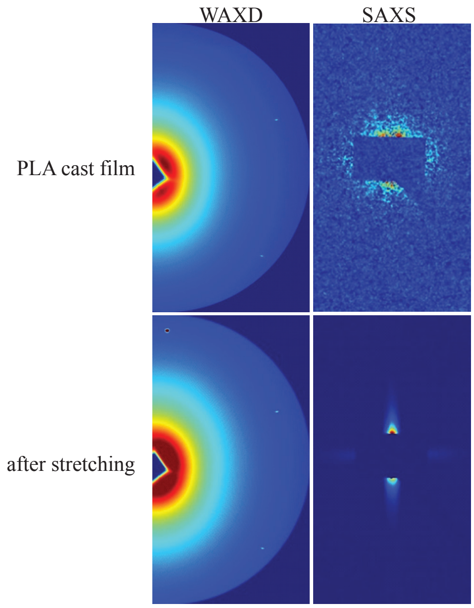

Figure 2: WAXD and SAXS patterns of the PLA cast film before and after stretching.

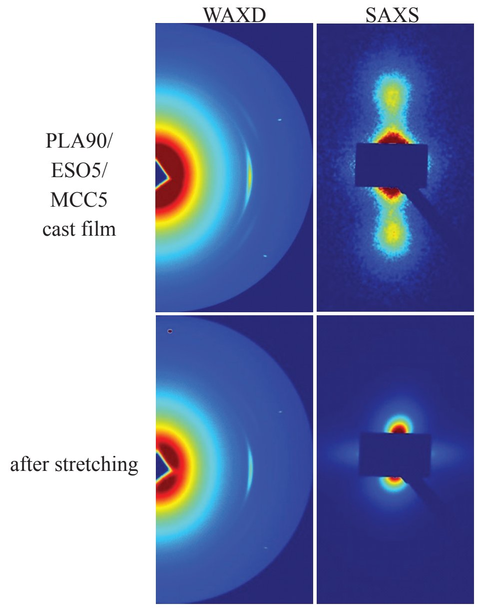

Figure 3: WAXD and SAXS patterns of the PLA90/ESO5/MCC5 film before and after stretching.

3.3 *Structural change of the PLA compounded film during stretching*

Post-processing is usually required after film forming. Structural change after stretching the film along a machine direction at room temperature was investigated. Figure 2 shows WAXD and SAXS patterns of the PLA cast film after stretching. The SAXS pattern showed a sharp pattern near a beam stopper but the WAXD pattern still gave blurred pattern. This meant that the stretching induced arrangement of PLA polymeric structure.

The PLA/ESO/MCC compounded film was stretched and the X-ray diffraction was measured as shown in Figure 3. The WAXD pattern of the film after stretching was rarely changed but the SAXS pattern gave only a clear pattern near a beam stopper similar to one of the PLA film after stretching. This confirmed that the microstructure was formed by stretching and the lamellar structure aligned in the stretching direction.

From overall measurement, the microstructure obtained in the cast film was summarized in Figure 4. After cast-film extruding, the PLA cast film composed of mainly amorphous structure. Addition of ESO assists polymeric chain movement and the PLA was aligned in the machine direction after extrusion. On the other hand, addition of MCC induces PLA crystallization without orientation as clearly observed in the WAXD pattern. When both ESO and MCC were mixed into the PLA film, the crystalline structure and the lamellar structure were arranged in the machine direction. After stretching along the machine direction of the film which is an example of post-processing, the polymer chains were oriented in the stretching direction but the crystal structure inside became more tilt than that before stretching.

4 Conclusion

The PLA cast film were prepared from a chill-roll cast film extruder. The microstructure was investigated by using synchrotron X-ray scattering technique. The PLA cast film obtained was in amorphous form. Addition of ESO and MCC enhanced chain mobility and crystal nucleation, thus, crystalline structure of PLA was created. Also, the crystalline structure was aligned along the machine direction. Post-processing such as stretching at room temperature induced chain alignment along the stretching direction. These results gives a guideline to control the microstructure evolution in the polymer processing which directly relates to the property of the final product.

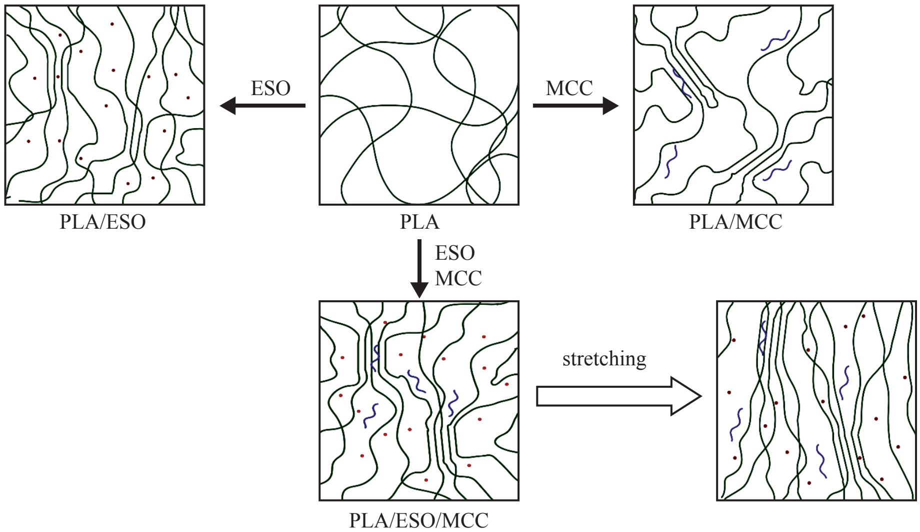

Figure 4: Schematic draw of the PLA compounded films taken at room temperature.

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