

Effect of the Addition of Nano-clay on the Physical Property and the Melt-Spinnability of Bacterial Polyester

Hideki Yamane^{1, a *}, Santa Momii¹, Shin-ichi Yagi², Isao Wataoka¹,
and Noriyuki Suzuki³

¹Kyoto Institute of Technology, Kyoto, Japan
²Kyoto Medical Planning, Co. Ltd, Kyoto, Japan
³Kaneka Corporation, Osaka, Japan

^ahyamane@kit.ac.jp

Keywords: Bacterial polyesters, Nano-clay, Mica, Physical properties, Melt-spinnability

Abstract. Synthetic mica organically treated with alkylamines was added to poly(3-hydroxybutyrate-co-3hydroxyhexanoate) (PHBH), one of the bacterial co-polyesters. Mica dispersing in PHBH acted as a crosslinking point of PHBH chains and increased the melt viscosity of PHBH significantly. The melt spinnability of PHBH was greatly improved by the addition of mica and the crystallization of PHBH in the spinline was highly promoted. WAXD spectra showed that the as-spun fibers of PHBH/MICA contain both highly oriented α - and β -forms of PHBH crystal. Further the SAXS revealed that the mica dispersing in the PHBH fiber oriented with its surface parallel to the fiber axis. The crystalline orientation of PHBH, orientation of mica, and the formation of β -form all improve the mechanical property of PHBH fibers.

Introduction

Poly(hydroxyl alkanoate) (PHA) is a bacterial bio-based polyester whose properties are similar to those of polypropylene [1]. Although various academic and industrial researchers have made a lot of efforts to obtain the fibers of PHA with a good mechanical property, the industrial production has not been succeeded yet. This is because of the very low crystallization rate of PHA and of the glass transition temperature lower than room temperature. On slowly cooling from the melt, PHA very slowly crystallizes and forms large spherulites. Rapid cooling results in an amorphous state and subsequently followed by the secondly spherulitic crystallization even at room temperature. This spherulitic structure of PHA and its copolymers makes as-spun fiber very brittle and makes cold deformation to enhance crystalline orientation extremely difficult [2, 3].

Various efforts have been paid to process PHA and its copolymers into fibers, films, and other products [4-11]. Most of these reports emphasize the effect of the nucleating agent on the crystallization of PHA in the spinline. When the molten PHA crystallizes in the spinline under tension, the PHA chains are more or less stretched and cause c-axis orientation to the fiber direction. The fibers with this sort of oriented crystal are rather ductile and can be cold drawn easily.

In this study, the organically treated mica was added to a bacterial copolyester and the effects of the addition of mica on various physical properties such as the crystallization behavior, the melt rheology, and the melt spinnability were examined. Further the mechanical property and the higher-order structure of the melt spun fibers were evaluated.

Experimentals

Materials. Synthetic Mica ME-100 was supplied by Co-op Chemical Co., Ltd., Tokyo, Japan. Alkylamines including octyl, lauryl, and stearyl amines were supplied by Nacalai Tesque and were used without further purification. The bacterial polyester used was poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) with a weight average molecular weight 5.4×10^5 and a 3-hydroxyhexanoate content 7 mol%.

Organic Treatment of Mica. Mica was dispersed in the ion exchanged water and kept stirring at 80°C. Alkyl amines were dissolved in the ion exchanged water and 6N HCl was added to it. Resultant alkyl ammonium salt aqueous solutions were added to the mica dispersion. Organically treated mica was precipitated after stirring for 3 hrs at 80°C. The precipitate was then washed several times with water and dried. 5 wt% of mica treated with various alkyl amines was mixed to the PHBH at a molten state.

Melt Spinning of the PHBH/MICA. The melt-spinning of PHBH/MICA was carried out at 160°C by using a laboratory size single screw extruder equipped with a 0.5 mm mono-hole die. The extrudate was stretched at room temperature and wound on the bobbin placed at 3 m below the die.

Measurements and Observations. The degree of the organic treatment was evaluated by FTIR. Morphology of the Mica was observed by using SEM after applying a gold coating. The layer distance of the mica was determined by WAXD and SAXS. Crystallization behavior of pure PHBH and PHBH/MICAs was observed with a polarized optical microscope equipped with a hot stage. The thermal property was determined with a DSC. The dynamic viscosity of PHBH/MICA melts was measured by using a rheometer (MR-300, REOROJI) with a parallel plates mode at 160°C. The higher-order structure and the mechanical property of the PHBH/mica fibers were determined with WAXD and by tensile tests, respectively.

Results and Discussion

Organic Treatment of Mica. The extent of the organic treatment was confirmed with IR spectra. Two peaks at 2,850 cm^{-1} and 2,920 cm^{-1} , identified as C-H stretching bands, appear on the IR spectra of the organically treated mica. A large peak detected around 3,450 cm^{-1} for untreated mica is attributable to the stretching vibration of -OH in water. This peak turned to be very small after the organic treatment indicating that the intercalation of alkyl amines made the mica rather hydrophobic. SEM observations revealed that although untreated mica has more or less bulky, organically treated mica tended to have a layered morphology. WAXD spectra also revealed that the organic treatment increased the inter-layer distance of mica and the mica treated with amines with longer alkyl chain has a larger layer distance as shown in table 1.

The Effect of the Addition of Mica on the Various Physical Properties of PHBH. 5 wt% of untreated mica and those treated with various alkyl amines were mixed to the PHBH at a molten state. First of all, the ability of mica as a crystallization nucleating agent at a static state was examined. Observation of the crystal growth by using a polarizing optical microscope under crossed Nicol at 110°C after quenching from the

Table 1 Layer distances of organically treated mica before and after mixing to PHBH

Alkylamine	Layer distance [nm]	
	As organically treated	in PHBH
Untreated	0.95	-
Octylamine	1.34	2.29
Laurylamine	1.57	2.80
Stearylamine	1.90	3.46

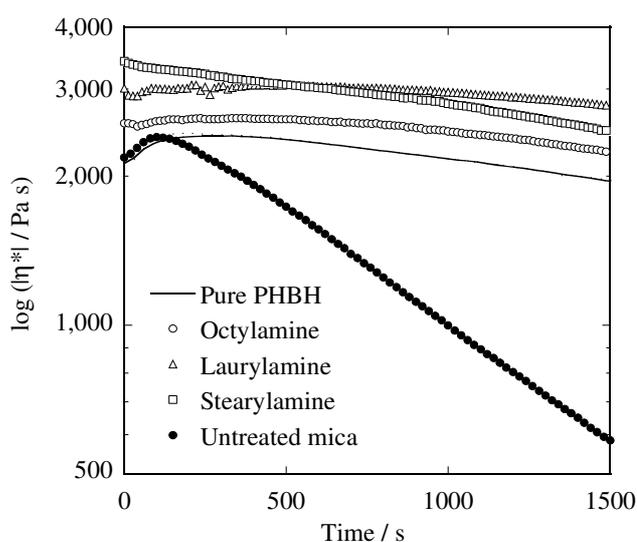


Fig. 1 Change in the melt viscosity of PHBH containing mica treated with various amines measured at 160°C.

molten state indicated that the addition of mica slightly promotes the crystallization of PHBH at a static state. This result suggests that although the mica acts as a nucleating agent, the effect is rather small at a static state.

Fig. 1 shows the change in the melt viscosity of pure PHBH and PHBH/MICAs with time measured at 160°C. The addition of mica increased the melt viscosity of PHBH comparing with that of pure PHBH. This may be due to the intercalation of PHBH chains into the mica layers acting as crosslinking points. It should be noted that the melt viscosity of PHBH containing untreated mica decreased significantly with time. This may be due to the hydrolytic degradation of PHBH by the water absorbed to the untreated mica.

Melt Spinnability and the Property and Structure of PHBH/MICA Fibers. Although the pure PHBH cannot be melt-spun at high take-up velocities, the addition of the organically treated mica significantly improved the melt-spinnability of PHBH. While pure PHBH melt spinline can be taken-up at 60 m/min at the maximum, those added with 5 wt% of organically treated mica can be taken-up at a velocity as high as 360 m/min. Besides the pure PHBH as-spun fiber was still in a molten state even on the bobbin and stuck together. On the other hand, all the PHBH/MICAs as-spun fibers were well crystallized in the spinline, irrespective of the length of the alkyl chain of the amines.

Higher-order Structure of the As-spun Fibers. It has been reported that homo poly(3-hydroxy butyrate) (PHB) is crystallized in a left-handed 2/1 helix conformation (α -form). In addition, a planar zigzag conformation (β -form) forms in some drawing and annealing conditions. The orthorhombic unit cell dimensions of α -form was $a = 0.576$ nm, $b = 1.320$ nm, and c (fiber axis) = 0.596 nm [12]. β -form shows only single, broad reflection at $2\theta = 19.7^\circ$ on the equator. Orts et al. suggested that the β -form crystallization takes place upon stretching of the amorphous tie chains between 2/1 helix α -form lamellae in the drawing process [13].

The as-spun fibers of PHBH/MICAs showed a highly oriented crystalline WAXD pattern as shown in Fig. 2. In addition to the reflections from α -form crystal with a 2/1 helix conformation, those from the β -form were also clearly observed on the equator. As Oats et al. suggested, β -form is generally observed for the highly drawn fibers. However PHBH/MICA as-spun fibers clearly showed the co-existence of α - and β -forms without applying a cold drawing process. Some of the PHBH chains were constrained between the mica layers and the crystallization under the constrained state produced the β -form.

Fig. 3 shows the SAXS patterns of the PHBH/MICAs.

The strong reflections from

the mica layer structure were detected on the equator of the SAXS pattern of as-spun fiber as well

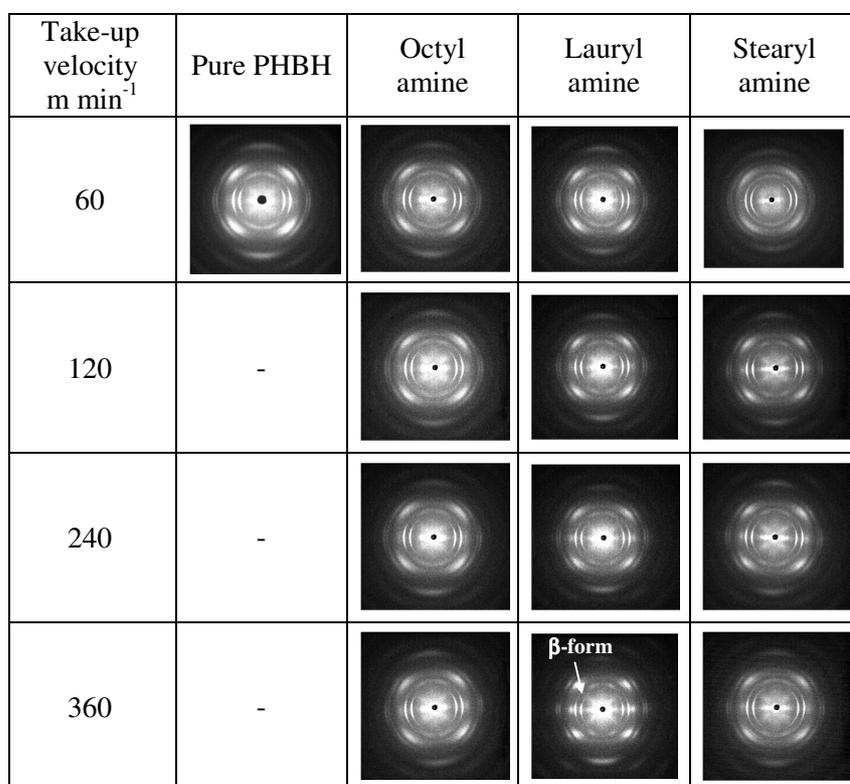


Fig. 2 WAXD pattern of the fibers of pure PHBH and PHBH/MICA fibers taken-up at various velocities.

as the scattering peaks from PHBH lamellar crystal around $2\theta = 1.8^\circ$ (long period). Since the reflection from mica layer concentrates on the equator of SAXS pattern, mica in the PHBH fiber is highly oriented with its surface parallel to the fiber axis. The reflections from mica layer indicate that the layer distance of mica was further increased after the mixing into PHBH as shown in table 1. Promotion of Crystalline orientation of PHBH and the orientation of mica with increasing take-up velocity improved the mechanical property of PHB/MICA fibers significantly.

Conclusion

The results obtained in this study suggest that the addition of organically treated mica does not simply increase the crystallization rate of PHBH as a nucleating agent. The crystallization of PHBH in the melt spinline is promoted by the molecular orientation given by the extensional stress in the spinline of the molten PHBH/MICAs higher than that of pure PHBH, although the mica does not promote the crystallization significantly at a static state. The spinline crystallization further improved the melt spinnability of PHBH. Some of the PHBH chains were constrained between mica particles and crystallized into β -form. The crystalline orientation of PHBH, the orientation of mica, and the formation of β -form all improved the mechanical property of PHBH fibers.

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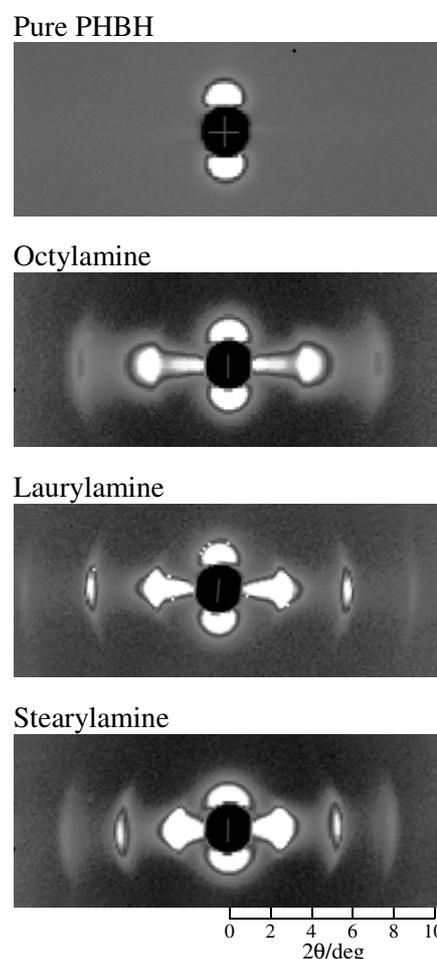


Fig. 3 SAXS pattern of the fibers of pure PHBH and PHBH/MICA.

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10.4028/www.scientific.net/AMR.970.308

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