



## The effect of epoxy-functionalized chain extender on crystal growth and morphology of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)

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### Abstract

The crystal growth rate of melt-crystallized poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) reacting with epoxy-functionalized chain extender was investigated by wide angle X-ray diffraction and polarized optical microscopy (POM). The maximum concentration of chain extender in this work was limited to 1.00 % *wt* for food contact considerations. The WAXD results revealed that the quantity of chain extender used in this study had no effect on crystal structure and all chain-extended PHBV had a PHB-type crystal structure. The rate of crystal growth determined from POM at various crystallization temperatures confirmed that the addition of epoxy-functionalized chain extender delayed the crystal growth rate but did not change the crystal growth process and morphology.

**Keywords:** PHBV, Epoxy-functionalized, Chain extender, Crystallization, Growth rate

### 1. Introduction

Poly (3-hydroxybutyrate-co-3-valerate) (PHBV), a biodegradable copolymer of polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV) produced commercially using bioengineering methods, possesses low gas transmission properties [1-2] and compostability [3] and thus has high potential for use in the packaging industry. However, its inherent thermal instability [4] is one of the main barriers in processing and applications.

Addition of a chain extender has been proposed to relieve this restriction. Dicumyl peroxide (DCP) was introduced to improve the poor thermal stability of PHBV. The branching and rheological behaviour of PHBV using low level of DCP was studied by Haene et al. [5] The increase in strain hardening with addition of higher amounts of DCP proved the branching of PHBV. Moreover, the cross-linking of PHBV using high levels of DCP was also studied by Fei et al. [6] The melt viscosity and mechanical properties of cross-linked PHBV were improved without compromising its biodegradability.

BASF Joncryl®, an epoxy-functionalized chain extender, has been proposed for polyester. The reaction between epoxide groups on the chain extender and carboxylic and hydroxyl end groups on polyesters [7-11], has led to the successful application of BASF Joncryl® on both petroleum-

based polyesters, such as poly(ethyleneterephthalate) (PET) [7, 12] and biodegradable polyesters, such as poly(lactic acid) (PLA) [10, 13-14]. BASF Joncryl® also showed promise for using with PHBV, because it improved thermal stability and increased complex viscosity of PHBV [15]. Nevertheless, the addition of this chain extender retarded rate of crystallization and hence care must be taken in solidification of the melt. The slow crystallization rate leads to stickiness of the PHBV sample during the processing caused by tackiness of the amorphous region [16]. Therefore, studies on crystallization will provide the necessary information to control and improve PHBV manufacturing. In this present work, the effect of an epoxy-functionalized chain extender on the crystallization behavior of PHBV was investigated by wide angle X-ray diffraction (WAXD) and polarized optical microscopy (POM).

### 2. Materials and methods

#### 2.1 Materials

Commercial PHBV pellet (HV = 3 mol%) was obtained by Tianan (Ningbo, China) under the trade name ENMAT™ Y1000P. The epoxy-functionalized chain extender ( $f_n > 4$  and epoxy equivalent rate = 285 g/mol) Joncryl® ADR-4368 S was supplied by BASF (Germany) in powder form.

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## 2.2 Extrusion process

The pellets of PHBV were dried in a vacuum oven at 100 °C for 120min before use, while chain extender was used as received. The samples of PHBV/chain extender were mixed by manually tumbling PHBV pellets with various amount of chain extender (0 - 1.00 wt%). The mixtures were compounded in the HAKKE Polylab twin screw extruder (Mess-Technic GmbH) fitted with a rod die ( $\phi = 6$  mm). The screw diameter was 24 mm and L/D ratio was 40. The screw speed was operated at 100 rpm corresponding to 8 min of average residence time determined with pigment tracing. The temperature profile was fixed at 180°C across all zones.

## 2.3 Wide angle X-ray diffraction (WAXD)

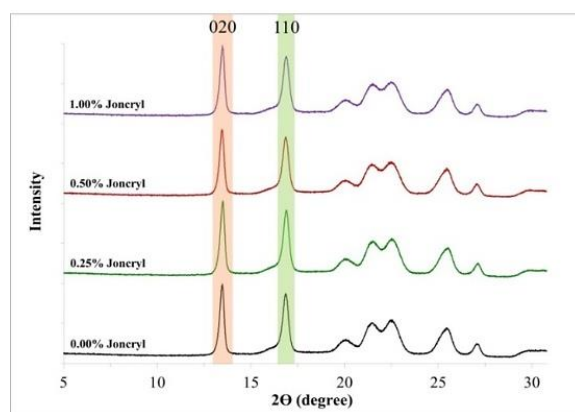
The crystalline phases were analyzed using X'Pert Pro MPD X-ray diffractometer (PANalytical) operating at 40 kV with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). The XRD data were recorded in the scattering angle range of  $2\theta = 5-55^\circ$  at room temperature.

## 2.4 Polarized optical microscopy (POM)

The crystal growth rate and spherulitic morphology of PHBV/chain extender were observed using an optical microscope (Axioskop40, Carl Zeiss) equipped with cross polarizers and hot stage (FP84HT, Metler Toledo) connected with control processor (FP90, Metler Toledo). A small piece of sample was sandwiched between two microscope coverslips and inserted in the hot stage. The sample was melted at 200 °C for 3 min to eliminate its thermal history and then rapidly cooled to the fixed crystallization temperature. The spherulitic morphology and the growth of spherulites were recorded using the equipped digital camera system. The crystal growth rate was determined from the slopes by plotting spherulite radius against crystallization time. The crystal growth rate was obtained as an average of ten spherulites for each sample.

## 3. Results and discussion

The wide angle X-ray diffraction was employed to investigate the effect of an epoxy-functionalized chain extender on the crystal forms of PHBV. The WAXD profiles of PHBV/Joncryl blends are displayed in Figure 1. All examined samples show the same pattern, with the two main diffraction peaks at 13° and 17° corresponding to (020) and (110) d spacings, respectively, indicating that all blends form PHB-type crystal structure [17-18].



**Figure 1** WAXD patterns of PHBV and its blends with Joncryl

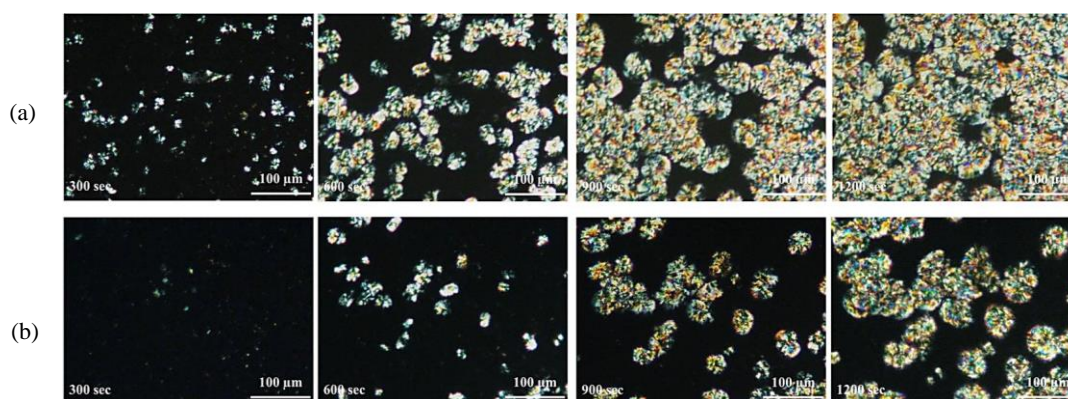
The lattice parameters  $a$  and  $b$  of PHBV and its blends are calculated from Figure 1 and summarized in Table 1. The values of both lattice parameters are very similar in all ratios, indicating that the concentration of the chain extender used in this study does not affect the crystal form of PHBV.

**Table 1** Thermal lattice parameters of PHBV/Joncryl blends

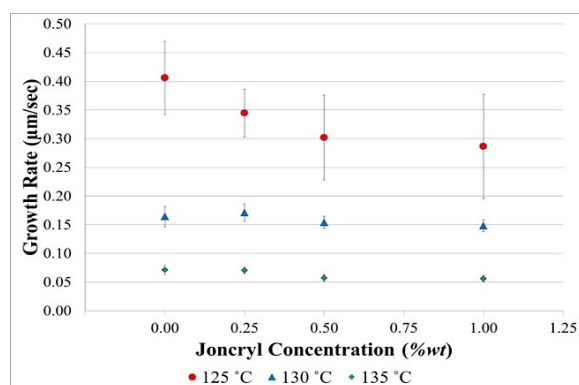
Joncryl concentration (%wt)	$a$ (Å)	$b$ (Å)
0.00	5.73	13.12
0.25	5.72	13.09
0.50	5.73	13.14
1.00	5.72	13.11

The crystal growth process of PHBV/Joncryl blends from molten state at a given temperature was also studied by polarizing optical microscopy. Figure 2 compares the growth process at 135 °C between PHBV and PHBV with 1.00 %wt Joncryl. The crystal growth rate of neat PHBV is faster than the rate of chain extended PHBV.

The crystal growth rates were clearly confirmed by plotting the crystal size against time. The crystal growth rates were determined from the slopes of the graphs. As seen in Figure 3, rising crystallization temperature leads to reduced crystal growth rate in all blends. The PHBV without Joncryl was used as reference and showed the highest growth rate in every crystallization temperature. Increasing the amount of the chain extender resulted in considerably decreasing crystal growth rate.



**Figure 2** POM images of the crystal growth process of (a) PHBV and (b) its blend with 1.00 %wt Joncryl at crystallization temperature of 135 °C



**Figure 3** Variation of crystal growth rates for PHBV/Joncryl blends at different crystallization temperatures

The change in tacticity of the molecules by the chain extender could explain the retardation of crystal growth. The effect of chain extender on crystallization behavior of poly(lactic acid) (PLA) as a function of tacticity was described by Zhong et al. [19]. The chain extender caused chain branching and depressed the tacticity of the PLA molecule. Only the unbranched chains crystallized in a short period, whereas the chains with branches crystallized at a later stage. This finding is in agreement with the result shown here.

On the basis of reaction between epoxy and carboxylic or hydroxyl groups [7-11], the epoxy groups of the chain extender used in this work would react with the –COOH and –OH end groups of the PHBV chains during the extrusion processing. As a result, two or even more PHBV chains subsequently combined together per one molecule of chain extender.

The morphologies in Figure 2 show the growth progress of PHBV and PHBV/Joncryl blend (1.00 % wt) spherulites at 135 °C. According to Lauritzen-Hoffman's nucleation theory, all samples show the regime II of crystallization, whereby many nuclei form and slowly grow [20]. Regime I is the case, where only one nucleus is formed on the surface and the layer forms completely before the next nucleus is active and regime III is the case where the nucleation rate is much larger than the spreading rate [20]. This was the case in every crystallization temperature employed in this study. Moreover, the information in Figure 2 also indicates that the ultimate form of the spherulitic structure of PHBV in regime II was generated from an axialite-like structure. At the initial stage of crystallization, the morphology is irregular and has axialite organization, then progresses into mature spherulites that finally impinge on each other. This phenomenon occurs in all chain extended PHBV, indicating that the addition of Joncryl did not affect the crystal growth process of PHBV.

#### 4. Conclusions

The effect of Joncryl chain extender on crystal growth and morphology of PHBV were investigated. The introduction of Joncryl did not change crystal structure, morphology or growth process of PHBV, indicating that Joncryl can be used as chain extender for PHBV without significant changes in its properties. However, special attention should be given when mixing PHBV with Joncryl, because of slow crystallization rate. Controlling the crystallization temperature might be the practical method to resolve the problem.

#### 5. Acknowledgements

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