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# MORPHOLOGIES AND KINETICS OF ISOTHERMAL CRYSTALLIZATION FOR GREEN POLYMER BLENDS COMPRISING PHBV AND ENR: INFLUENCE OF RUBBERY PHASE

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#### ABSTRACT

Isothermal crystallization behavior and morphologies were studied for green polymer blends of poly(R-3-hydroxybutyrate-co-R-3-hydroxyvalerate) (PHBV) and epoxidized natural rubber (ENR). Polarizing optical micrographs reveal the immiscibility of the systems in the molten state. Exponential decay of the rates of crystallization with ascending isothermal crystallization temperatures ( $T_c$ ) is observed for both neat PHBV and PHBV in the blends. Besides, the rates of crystallization of PHBV decrease with increasing ENR content at  $T_c = const$ . Rubbery phase of ENR influences the crystallization behavior of PHBV which in turn affects morphology formation in these blends. These blends with biodegradable and elastic properties are proposed to be potential packaging material.

Keywords: isothermal crystallization, morphology, poly(R-3-hycroxybutyrate-co-R-3-hydroxyvalerate), epoxidized natural rubber

#### INTRODUCTION

Blending of polymers is a versatile technique because it allows for fine tuning of the properties of materials by compositional change. It is an alternative approach for generating new materials as compared to direct synthesis of new polymers with desired properties. Blends of thermoplastic and elastomer have been studied extensively 1-5. Knowledge on thermal properties of these systems is important for efficient adjustment of structure-property relationships. Phase morphology formation in these blends is strongly coined by thermal behaviors of the constituents. Properties of the materials are ruled by the composition of the blends and the interaction between the constituents at narrow interfacial region, which can be reflected in the thermal properties of the blends. The purpose for the blending in these cases points towards two directions: i) toughening the matrix of the thermoplastic with dispersed phase of the elastomer and ii) increase the strength of the elastomer matrix with dispersed phase of the thermoplastic.

Due to growing environmental awareness and concerns over the sustainable availability of the crude oil in the future, the industry and academia have been intensively working on polymeric materials which function as renewable natural resources. On top of this, biodegradability of the materials is emphasized. Poly(R-3hydroxybutyrate-co-R-3-hydroxyvalerate) (PHBV) is synthesized by controlled bacterial fermentation <sup>6</sup>. PHBV is a biodegradable aliphatic polyester and displays high crystallinity <sup>2, 7</sup>. The *in vivo* application of PHBV may be limited because of its hydrophobic characteristic with no bioactive fragments. Functional groups or biomacromolecules may be immobilized on the PHBV for direct tuning of chemical functionality on the surface without changing the bulk properties of the PHBV 8, 9. The cell-biomaterial interaction, which influences cell proliferation, migration and differentiation, may be regulated by modification of the chemical functionality of the surface. PHBV is miscible with poly(ethylene oxide)  $^{10}$  and poly(R-3hydroxybutyrate) <sup>7</sup> but immiscible with poly( $\varepsilon$ -caprolactone) <sup>11</sup> and epoxidized natural rubber (ENR) <sup>2</sup> by morphological studies as well as thermal analysis.

ENR is produced by epoxidation of natural rubber (NR) where the double bond of the isoprene unit reacts with peracid and forms epoxide group during the epoxidation process. ENR retains most of the properties of NR with additional interesting properties, such as enhanced oil resistance, polarity, elasticity, abrasion resistance and decreased gas permeability <sup>12</sup>. The increase in the polarity of the ENR as compared to that of NR is due to the presence of the oxirane group. ENR is suggested to have specific interaction with poly(vinyl chloride) <sup>13-15</sup> and melt reaction with poly(hydroxyalkanotes) <sup>1, 16</sup> and poly(ethylene-*co*-acrylic acid) <sup>17, 18</sup>.

In this study, PHBV with 12 mol% of hydroxyvalerate content is blended with ENR with 50 mol% of epoxide content. These blends form immiscible systems. The introduction of PHBV into the matrix of ENR may enhance the mechanical properties (e.g. tensile strength) of ENR. On the other hand, incorporation of ENR into the matrix of PHBV shall introduce elasticity to the blends. As mentioned before, thermal properties of the blends are reflective of the development of phase morphologies. Morphology becomes one of the crucial factors that affects the mechanical behavior of the immiscible blends. In blends where the PHBV is in excess, this component crystallizes out from the melt comprising a dispersion of ENR domains. At the opposite side of the composition scale, ENR being in excess, PHBV domains will develop in the ENR matrix. Therefore, it is necessary to study the crystallization behavior of PHBV in these heterogeneous blends and the resulting morphology formation under isothermal conditions. The influence of the morphology on the mechanical behavior of the blends will be discussed in a forthcoming paper.

#### EXPERIMENTAL

#### Materials

PHBV [weight average molecular weight  $(M_w) = 2.38 \cdot 10^5$  g mol<sup>-1</sup> and number average molecular weight  $(M_n) = 1.09 \cdot 10^5$  g mol<sup>-1</sup>] was purchased from Aldrich Chemical Co. (St. Louis, MO, US). ENR  $(M_w =$  $7 \cdot 10^5$  g mol<sup>-1</sup> and  $M_n = 2 \cdot 10^5$  g mol<sup>-1</sup>) was supplied by Rubber Research Institute (RRI), Sungai Buloh, Malaysia. Quantities  $M_w$  and  $M_n$  were estimated by gel permeation chromatography (GPC) at 30 °C using a Waters GPC (Milford, US). PHBV and ENR were purified by dissolving in chloroform (Fisher Scientific, Loughborough, UK), and were precipitated in methanol and afterwards filtered off and dried in vacuum oven at 50 °C for 24 hr. Both were utilized after purification. The drying duration of 24 hr in vacuum oven was found to be sufficient for complete drying of the materials.

#### **Preparation of the Blends**

Thin films of the PHBV/ENR were prepared by casting from 1 % (w/w) solution of the two components in chloroform (Fisher Scientific, Leicestershire, UK) followed by evaporation of the solvent at approximately 30 °C overnight. The sample was then dried at 50 °C under vacuum for 24 hr.

#### Polarizing optical microscopy (POM)

Morphologies of blends during molten state and after complete isothermal crystallization were studied using Image-Pro Express software which was attached to the Nikon microscope (Yokohama, Japan) equipped with a Linkam heating/cooling unit (Linkam TM 600/s) (Surrey, UK). Samples were annealed at annealing temperature ( $T_{a}$ ) = 175 °C for 1 min and micrographs were captured

Int J Pharm Pharm Sci, Vol 3, Suppl 1, 1-6

in the molten state of the samples. Then, the samples were cooled at 20 °C min<sup>-1</sup> to selected crystallization temperature ( $T_c$ ) = 112 °C and held until complete crystallization. Micrographs were captured at the selected  $T_c$  after 60 min. At least 3 micrographs were captured at different spots of the samples to ensure that the analysis was based on a representative region of the samples.

#### Differential scanning calorimetry (DSC)

Perkin-Elmer DSC 7 (Shelton, CT, US) was used to study the isothermal crystallization behavior of PHBV for the blends. The DSC was calibrated with indium and zinc standards and nitrogen gas was purged throughout the analysis to minimize thermo-oxidative degradation. Samples with weight around 10 mg were used for each DSC experiment. Samples were annealed at  $T_a = 175$  °C for 1 min, followed by cooling at a rate of 20 °C min<sup>-1</sup> to the respective  $T_c$  and held until complete crystallization. The half time of crystallization ( $t_{0.5}$ ) was determined at  $T_c = const$ . The range of isothermal crystallization temperature is from 105 to 112 °C.

The errors of the parameters after Hoffman's Arrhenius-like relationship [c.f. Eq. (1)] are just the errors of the regression calculations. Regression calculations are made from DSC experiment at  $T_c$  = *const*. The confidence intervals for the parameters after Hoffman's Arrhenius-like relationship refer to the regression analysis based on 2-tailed student *t*-test at 95 % confidence level.

## **RESULTS AND DISCUSSIONS**

### **Blend morphologies**

Figure 1 shows selected examples of morphologies that developed in PHBV and the blends of PHBV and ENR in molten state as well as after complete isothermal crystallization at  $T_c$  = 112 °C. Volumefilling spherulites grow in neat PHBV at  $T_c = 112 \text{ °C}$  [Figure 1 (d)] and only one phase can be observed for molten PHBV at  $T_a = 175 \text{ °C}$ [Figure 1 (a)]. Two phases can be clearly seen in the molten state at  $T_a = 175$  °C for the immiscible PHBV/ENR 80/20 and 50/50 blends in Figures 1 (b) and (c), respectively. This is in agreement with the experimental results of glass transition temperature for blends of PHBV and ENR as demonstrated in ref. (2), which reveal the immiscibility of the constituents. Volume-filling spherulites grow in PHBV/ENR 100/0 to 70/30. The crystallization of PHBV at  $T_c = 112$ °C as the matrix in the blends is not without any disruption from ENR although PHBV and ENR are physically separated. The growing front of the PHBV spherulites can not reject ENR efficiently, leading to fine intraspherulitic dispersion of ENR in PHBV even at ENR content as low as 20 wt% [c.f. Figure 1 (e)]. This may be the attributing factor of the decrease in the rate of crystallization of PHBV in the immiscible blends with ascending ENR content at  $T_c = const$ which will be discussed in the following section. Fine dispersion of ENR coalesces to bigger islands at 50 wt% of ENR [c.f. Figure 1 (f)] with intra- as well as interspherulite dispersions. Phase inversion can be seen at mass fraction of ENR  $\ge 60$  wt% (figure is not shown).







(d)



(b)



(e)

Int J Pharm Pharm Sci, Vol 3, Suppl 1, 1-6



Fig. 1: Morphology of PHBV/ENR blends

Molten blends at  $T_a = 175 \text{ °C}$  and micrograph was captured at temperature of the POM at 175 °C: (a) 100/0, (b) 80/20 and (c) 50/50.

Isothermally crystallized at  $T_c = 112$  °C after complete crystallization and micrograph was captured at temperature of the POM at 112 °C: (d) 100/0, (e) 80/20 and (f) 50/50.

Magnification: 40 X. The bar corresponds to 25 µm.

#### Kinetics of isothermal crystallization of PHBV

The overall rate of isothermal crystallization was monitored by thermal analysis through the evolution of enthalpy of crystallization by DSC as described in Experimental section. Figure 2 shows the DSC traces of isothermal crystallization for neat PHBV at different  $T_cs$  as well as for PHBV/ENR 50/50 at  $T_c$  = 112 °C. Figure 2 shows qualitatively the reduction of the crystallization rate of neat PHBV

with increasing  $T_c$  as well as with increasing content of ENR at  $T_c$  = 112 °C. Half time of crystallization ( $t_{0.5}$ ), which is the time taken for 50 % of the crystallinity of the crystallizable component to develop, is estimated from the area of the exotherm at  $T_c$  = *const*. The rate of crystallization of PHBV in ENR blends can be easily characterized by the experimentally determined reciprocal half time, ( $t_{0.5}$ )<sup>-1</sup>. The results for neat PHBV may serve as reference for evaluation of crystallization of PHBV in the blends.



Fig. 2: DSC traces of isothermal crystallization for PHBV/ENR 100/0 at *T*<sub>c</sub>: (a) 105, (b) 108 and (c) 112 °C and (d) PHBV/ENR 50/50 blend at *T*<sub>c</sub> = 112 °C. Curves were displaced for better identification.

In general, for immiscible thermoplastic elastomer blends, when the matrix of the blends is the crystallizable constituent, the crystallization kinetics for the semiscrystalline polymer in the blends are in close approximation to the neat semicrystalline polymer. On the other hand, the crystallization kinetics of the discrete droplets of the semicrystalline polymer in an amorphous matrix may be markedly influenced as compared to that of the neat semicrystalline polymer. However, the fine intraspherulitical dispersion of ENR in PHBV matrix as observed in Figures 1 (e) and (f) has led to the slight deviation of the mentioned general principles of the crystallization kinetics for immiscible thermoplastic elastomer blends. The rates of crystallization of PHBV reduce gradually with

Int J Pharm Pharm Sci, Vol 3, Suppl 1, 1-6

ascending content of  $\ensuremath{\mathsf{ENR}}$  in the blends even when  $\ensuremath{\mathsf{PHBV}}$  is in excess.

Figure 3 demonstrates semilogarithmics plots of rates of crystallization of PHBV in ENR blends versus crystallization temperatures [correlation coefficients (*r*) for all curves are > 0.99]. Within this range of crystallization temperatures, the rates of crystallization of neat PHBV as well as the PHBV in the blends decrease exponentially with ascending crystallization temperatures. The rates of crystallization of PHBV in blends also decrease with ascending ENR content at  $T_c = const$ . This is due to the intraspherulitical entrapment of dispersed regions of ENR in the growing spherulites of PHBV.



**Fig. 3: Rate of isothermal crystallization of PHBV in the blends as a function of crystallization temperature.** PHBV/ENR blends: •  $-100/0, \times -80/20, \square -60/40, \circ -50/50$  and  $\blacktriangle -30/70$ .



Fig. 4: Normalized crystallinity (X) versus crystallization time for PHBV in the blends at  $T_c = 112 \text{ °C}$ .

Int J Pharm Pharm Sci, Vol 3, Suppl 1, 1-6

(2)

PHBV/ENR blends: • – 100/0, × - 80/20, □ – 60/40, ∘ – 50/50 and ▲ – 30/70.



Fig. 5: Normalized crystallinity (X) versus reduced time of crystallization for PHBV in the blends at  $T_c = 112 \text{ °C}$ .

PHBV/ENR blends: ○ – 100/0, × - 80/20, □ – 60/40, ◊ – 50/50 and Δ – 30/70.

Figure 4 shows the normalized crystallinity (*X*) as a function of crystallization time (*t*) for PHBV in the blends at  $T_c = 112$  °C. Quantity *X* at time *t* is defined as the ratio of the extent of crystallization at time *t* and the complete crystallization at  $T_c = const$ . The growing rates of PHBV spherulites in the blends slow down with increasing ENR content. These different curves coincide and form a master curve to a good approximation when the normalized crystallinities are plotted versus the reduced times of crystallization ( $t/t_{0.5}$ ) as illustrated in Figure 5. This suggests that the overall features of the crystallization of PHBV in the blends do not show significant variation with the composition of the blends.

#### Temperature dependence of the crystallization rate

The temperature dependence of the crystallization rate of PHBV in the blends is discussed in terms of Hoffman's Arrhenius-like relationship as depicted in Eq. (1)<sup>19</sup>.

$$(t_{0.5})^{-1} = const \exp\left(-\frac{B}{\Delta T_c}\right)$$
<sup>(1)</sup>

Quantity B might be related to the ratio of energy densities in lamella fold surface and bulk formulated with the use of Kelvin equation as shown in Eq. (2)

$$B = \frac{2T_{\rm m}^{\rm o}}{\gamma} \frac{\left(\sigma/l_{\rm c}\right)}{\rho \Delta H_{\rm spec}}$$

where  $(\sigma/l_c)$  marks surface energy density of a lamella grown at crystallization temperature  $T_c$  and it acts as the driving force for crystallization of PHBV in the blends. Quantities  $\sigma$ ,  $l_c$ ,  $\rho$  and  $\Delta H_{spec}$ denote surface tension, finite thickness of lamella at  $T_c$  density and the specific enthalpy of melting, respectively. The equilibrium melting temperature ( $T_m^o$ ) was determined after Hoffman-Weeks method  $^{20}$  where linear relationship between  $T_c$  and the corresponding melting temperature ( $T_m$ ) of PHBV in the blends is observed (2). Parameter  $\gamma$  represents the change of melting temperature with crystallization temperature,  $dT_m/dT_c$ , after Hoffman-Weeks plots. Undercoolings ( $\Delta T_c$ ) of PHBV in the blends can be approximated to  $\Delta T_c \equiv T_m^o - T_c$ .

An exponential decay of the rates of crystallization of PHBV in the blends with increasing  $(\Delta T_c)^{-1}$  is recognized as shown in Figure 6 (r for all curves are > 0.991). In other words, the rates of crystallization of PHBV in the blends dramatically decrease when the crystallization temperatures are approaching the equilibrium melting temperature. Values of  $T_{m^0}$  and  $\gamma$  are extracted from ref. (2). Values of the parameter B and the ratio of energy densities evaluated after Eqs. (1) and (2) are listed in Table 1.



Int J Pharm Pharm Sci, Vol 3, Suppl 1, 1-6

Fig. 6: Rate of isothermal crystallization of PHBV in the blends as a function of reciprocal undercooling.

#### PHBV/ENR blends: • − 100/0, × − 80/20, ■ − 60/40, ○ − 50/50 and Δ − 30/70.

PHBV/ENR blends	<i>B /</i> K	$rac{\left(\sigma/l_{ m c} ight)}{\left( ho\Delta H_{ m spec} ight)}$
100/0	831 ± 61	$0.41 \pm 0.03$
80/20	735 ± 37	$0.38 \pm 0.02$
60/40	883 ± 96	$0.42 \pm 0.05$
50/50	816 ± 106	$0.39 \pm 0.05$
30/70	966 ± 54	$0.47 \pm 0.03$

Table 1: Parameter B and ratio of energy densities determined after Eqs. (1) and (2)

The values of the energy ratio  $\left[\frac{(\sigma/l_c)}{(\rho\Delta H_{\rm spec})}\right]$  indicate that the PHBV crystallite has relatively high interfacial tension with the

crystallite has relatively high interfacial tension with the surrounding amorphous ENR at all compositions as compared to that of the PET in blends with ENR <sup>21</sup>. This leads to the formation of large spherulites with ENR regions-included in the PHBV crystalline regions (c.f. Figure 1). As a consequence, addition of ENR into PHBV progressively slows down the rate of crystallization of PHBV in the blends even though PHBV/ENR blends are immiscible.

## CONCLUSION

The study presents morphologies and kinetics of isothermal crystallization of PHBV in blends with ENR. Morphologies of the blends in the molten state suggest that these blends are immiscible. Correlation of interfacial adhesion exists between the narrow interfacial region, which may develop between PHBV and ENR phases, with the ratio of energy densities in surface and bulk of the crystallites is proposed. It turns out that PHBV phase shows relatively strong affinity for ENR phase. Hence, fine intraspherulitical dispersion of ENR in PHBV spherulites can be observed when the content of PHBV is in excess. The rates of crystallization of PHBV in the blends gradually decrease with ascending content of ENR because the growing PHBV spherulites can not reject the ENR.

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Int J Pharm Pharm Sci, Vol 3, Suppl 1, 1-6