Partially bio-based thermoplastic elastomers by physical blending of poly(hydroxyalkanoate)s and poly(ethylene-co-vinyl acetate)

P. Ma^{1,2,3*}, X. Cai⁴, M. Chen^{1,2}, W. Dong^{1,2}, P. J. Lemstra³

¹The Key Laboratory of Food Colloids and Biotechnology of Ministry of Education, 1800 Lihu Road, 214122 Wuxi, China.

²School of Chemical and Material Engineering, Jiangnan University, 1800 Lihu Road, 214122 Wuxi, China.

³Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, 5612 Eindhoven AZ, the Netherlands.

⁴School of Food Science and Technology, Jiangnan University, 1800 Lihu Road, 214122 Wuxi, China

Received 16 January 2014; accepted in revised form 19 March 2014

Abstract. Partially bio-based thermoplastic elastomers (bio-TPE) were designed and prepared by physical blending a commercial grade poly(hydroxyalkanoate)s (PHBM, Metabolix) and poly(ethylene-co-vinyl acetate) (EVA). The PHBM is miscible with EVA90 which has a vinyl acetate (VA) content of 90 wt% while it is not miscible with EVA at low VA content (≤ 70 wt%). The PHBM/EVA90 blends exhibit high tensile strength and typical thermoplastic elastomeric characteristics e.g. high elongation at break ($>800\%$), good strain-recovery ($>60\%$) and melt processability. The spherulite growth rate of PHBM decreases with increasing EVA90 content. Consequently, a large number of fine PHBM spherulites were formed in the blends. The spherulites act as physical crosslink-points leading to a thermoreversible network in the blends. Such network and elastic EVA90 molecules result in the thermoplastic and elastomeric characteristics of the PHBM/EVA90 blends.

Keywords: polymer blends and alloys, poly(hydroxybutyrate), poly(ethylene-co-vinyl acetate), miscibility, thermoplastic elastomer

1. Introduction

Polymers that derived from biomass have received considerable attention due to the sustainability issue and environment concern. Poly(hydroxyalkanoates) (PHAs) are synthesized and accumulated intracellularly by a number of micro-organisms [1, 2]. The best-known PHA is poly(3-hydroxybutyrate) (PHB) discovered in *Bacillus megaterium* by Lemoigne in 1926 [3]. PHB is a semi-crystalline thermoplastic with niche applications due to its biocompostability under both aerobic and anaerobic conditions, biocompatibility and renewable nature [4]. The mechanical and thermal properties of PHB are similar to those

of poly(propylene). However, poly(propylene) cannot be substituted by PHB yet since there are many drawbacks which limit the applications of PHB, e.g. high production cost, poor processability and brittleness.

The brittleness of PHB is ascribed to large spherulites and cracks inside of the spherulites [5]. Consequently, PHB has low elongation at break ($\epsilon_b \sim 3\%$) and low impact toughness ($\sigma_i \sim 2$ kJ/m²) [6]. Techniques such as synthesis of PHB copolymers by biological modification [7–9], blending [6, 10–14] and improvement on processing conditions [15, 16] have been developed to minimize the drawbacks.

*Corresponding author, e-mail: pimingma@hotmail.com

© BME-PT

Synthesis of PHB copolymers could improve the toughness but compromise the strength and crystallization rate. On the other hand, blending is preferably used to toughen PHB.

The toughness of PHB could be improved by incorporation of rubbers. The σ_i was increased by 440% after addition of epoxy natural rubber using maleated-poly(butadiene) as a compatibilizer [10]. The ϵ_b of PHB was increased to 10% after addition of 20 wt% poly(hydroxyoctanoate) accompanied by a considerable reduction in tensile strength, crystallization temperatures (T_c) and melting temperatures (T_m) [11]. The ϵ_b of PHB was even increased by a factor of 50 after addition of cellulose nanowhiskers using poly(ethylene glycol) as a plasticizer [12]. In another study, the ductility of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV, HV content = 12 mol%) was considerably enhanced by incorporation of 20 wt% bisphenol-A (BPA) ascribing to a formation of hydrogen bond network between the two components [13]. The yield stress and ϵ_b of the PHBV/BPA (80/20, wt/wt) blend were reported to be 16 MPa and 370% respectively. In our previous study, both ϵ_b and σ_i of PHB were increased by melt blending with biodegradable copolymers, i.e. poly(d,l-lactic acid) and poly(butylene succinate). The ϵ_b and σ_i were further improved via *in situ* compatibilization using peroxide as a free radical initiator [6, 14].

Blending is an effective and economic route to improve mechanical properties of polymers, however the toughness of PHB was only increased to a certain extent by blending with immiscible (co-)polymers. Some miscible (co-)polymers were blended with PHB in literatures such as poly(methyl methacrylate) [17], poly(ethylene oxide) [18] and poly(vinyl acetate) [19]. However, the effect of the miscible (co-)polymers on the mechanical properties of PHB was rarely studied. PHB-based thermoplastic elastomer (TPE) was even less reported.

The prime objective of this paper is to provide a method to prepare partially bio-based thermoplastic elastomers by physical blending PHBM and poly(ethylene-co-vinyl acetate) (EVA) copolymer. In the first part, the effect of vinyl acetate (VA) content on the miscibility, morphology and mechanical properties of the PHBM/EVA blends were investigated. In the second part, mechanical properties and morphology of the miscible PHBM/EVA blends were studied in detail and a mechanism for the thermoplastic elasticity was proposed based on the relation between

properties and morphology. The thermoplastic elastomeric behavior of PHBM via melt blending with EVA, to the best of the authors' knowledge, has not been reported yet, which might broaden the application range of this polymer.

2. Experimental details

2.1. Materials

Commercial grade poly(hydroxyalkanoate)s (Mirel™ M6000) was supplied by Metabolix, Inc. USA, which is a mixture of poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-4-hydroxybutyrate). Since the two components are miscible, the mixture shows single phase morphology and thus is referred to as PHBM in this paper. EVA copolymers (Levapren® EVM) with VA contents from 40 to 90 wt% were supplied by Lanxess Chemical Co., Ltd.. The EVA with VA content of x wt% is coded as EVAx in this paper. The parameters of each grade EVA are shown in Table 1. Behenamide (analytical standard) as a nucleating agent was purchased from Fluka. All the materials were used as received.

Table 1. Characteristics of EVA copolymers

Sample code	VA content [wt%]	Mooney viscosity ^a ML (1+4) 100°C [MU]	Density [kg/m ³]	T _g ^b [°C]
EVA40	40±1.5	20±4	980	-32
EVA50	50±1.5	27±4	1000	-29
EVA60	60±1.5	27±4	1040	-28
EVA70	70±1.5	27±4	1080	-20
EVA90	90±2.0	38±6	1150	14

^aTested according to IS289/ASTM D 1646.

^bMeasured by DSC at a heating rate of 10°C/min.

2.2. Blend preparation

The PHBM and EVA copolymers were dried at 50°C in a vacuum oven for 12 hours before use. PHBM/EVA blends with 0.5 wt% of behenamide based on the weight of PHBM were prepared in a twin-screw mini-extruder at 170°C for 3 min. The speed of screw was 90 rpm.

Two series of blends were studied:

- PHBM/EVA (80/20, wt/wt) blends with varying the VA content in EVA copolymers from 40 to 90 wt%;
- PHBM/EVA90 blends with compositions of 100/0, 90/10, 80/20, 70/30, 50/50, 30/70 and 0/100 (wt/wt).

The extrudates of PHBM/EVA blends were compression-molded into sheets (0.6 mm in thickness) at 175°C for 2 min and then cold compression-

molded for 15 min. The compression-molded samples were used for further characterizations. It has to be addressed that the degradation of PHBM/EVA blends under the above processing conditions were not so serious as evidenced by a relatively stable torque values of the mini-extruder as a function of processing time.

2.3. Characterizations

Scanning electron microscope (SEM): SEM (Quanta 600-F-ESEM, FEI, the Netherlands) was used to characterize the phase morphology of the PHBM/EVA blends. The samples were first cryo-microtomed at -80°C with a diamond knife and then sputter-coated with a thin gold layer at 65 mA for 45 seconds before observation.

Transmission electron microscope (TEM): TEM was performed on the PHBM/EVA90 (80/20, wt/wt) samples using a Tecnai 20 microscope, operated at 200 kV. Ultrathin sections (~ 100 nm) were prepared at -80°C using a Leica Ultracut S/FCS microtome. No staining was applied because PHBM and EVA copolymers have enough electron density contrast according to our previous study.

Two types of mechanical behavior were studied at room temperature:

- Universal tensile properties of the samples were measured by using a Zwick Z100 tensile tester at a crosshead speed of 10 mm/min. The narrow parallel-sided portion of the dumbbell-shaped tensile bar was 12 mm in length, 0.6 mm in thickness and 2 mm in width.
- Hysteresis cycle tests were performed on the same tensile tester. The dumbbell-shaped tensile bar was first stretched to 500% elongation with no hold time imposed at extension, after which the crosshead direction was immediately reversed to 170% elongation. The cross-head speed of stretching and recovering is 10 mm/min. Three repeating cycles were tested.

Dynamic mechanical analysis (DMA): DMA was carried out on a DMAQ800 (TA Instruments, USA) with a tensile-film mode. The specimens ($13.0 \times 6.5 \times 0.6$ mm³) were measured from -60 to 170°C at a frequency of 1 Hz, with a constant amplitude of 10 μm and a temperature ramp of $3^{\circ}\text{C}/\text{min}$. The storage modulus and loss modulus were recorded as a function of temperature.

Differential scanning calorimetry (DSC): DSC analysis is performed on a DSC Q1000 (TA Instruments,

USA). The samples were heated from -50 to 190°C . The first heating DSC scans were recorded and the glass transition temperatures (T_g) were obtained from the first heating DSC curves.

Polarized optical microscope (POM): Thin films of PHBM/EVA blends were cryo-microtomed from the compression-molded sheets. The spherulite morphology of each film was observed by using a Zeiss LM Axioplan microscope under polarization mode. The spherulite growth rate (G) of PHBM was measured by using the microscope in combination with a Linkam hot stage. Thin film of each sample was first heated to 190°C to erase thermal history, then quenched to designed temperatures, i.e. 70 – 130°C at a cooling rate of $60^{\circ}\text{C}/\text{min}$, and kept at the designed temperatures for isothermal crystallization. The radii of the spherulites (r , [μm]) were recorded as a function of time (t , [min]). The spherulite growth rate (G) was obtained via equation $G = \Delta r / \Delta t$.

3. Results and discussion

3.1. Effect of VA content on the miscibility and morphology of PHBM/EVA blends

A first insight in miscibility and phase separation of two (co-)polymers is comparing their solubility parameters (δ). Two polymers may show miscible behavior if their solubility parameters are close to each other. An example is about poly(vinyl acetate) (PVAc) and PHBM whose solubility parameters are 9.6 and 9.1 (cal/cm³)^{1/2} respectively [20]. The solubility parameters of the EVA copolymers vary between the δ of LDPE (8.3 (cal/cm³)^{1/2} [20] and the δ of PVAc depending on composition. Thus, the miscibility between PHBM and EVA could be tuned by varying composition of the EVA copolymers.

The miscibility of polymers can be indicated by analysis of the glass transition temperatures (T_g) in their blends. The storage modulus (E') and loss modulus (E'') of the PHBM/EVA blends from dynamic mechanical analysis (DMA) are presented in Figure 1. The peak temperatures of the E'' are referred to as T_g of the corresponding components. The neat PHBM and the PHBM/EVA90 (80/20, wt/wt) blend show single T_g of -1.3 and 8.3°C respectively. Each of the other samples displays two separate T_g , one for the PHBM phase ($T_{g\text{-PHBM}}$) and the other for the EVA phase ($T_{g\text{-EVA}}$), as noted in Figure 1. The glass transition temperatures of the PHBM/EVA90 blends were investigated as a function of EVA90 content, as shown in Figure 2. Only single T_g is detected for

Figure 1. Storage modulus (E') and loss modulus (E'') of the PHB and the PHB/EVA (80/20, wt/wt) blends. The E'' curves were shifted in the y axis to avoid overlaps.

Figure 2. Glass transition temperatures (T_g) of the PHB/EVA90 blends as a function of EVA90 contents. The T_g is measured by using DSC and DMA respectively

each PHB/EVA90 blend. Moreover, the T_g shows strong dependence on compositions. These results indicate that PHB is thermodynamically miscible with EVA90 but is immiscible with the other EVA

copolymers. The values and variation trend of the storage modulus (E') of the PHB are slightly affected by addition of 20 wt% of the EVA copolymers since PHB is a matrix.

a)

b)

c)

d)

Figure 3. SEM images (scale bar = 5 μm) of the PHB/EVA (80/20, wt/wt) blends as a function of VA contents: (a) 40 wt%, (b) 50 wt%, (c) 70 wt% and (d) 90 wt%. The EVA domains are indicated by arrays in PHB matrix. The slight orientation of the morphology in these images is resulted from section-preparation (microtome). A TEM image of the PHB/EVA90 (80/20, wt/wt) is shown as an inset in image d.

The morphology of PHBM/EVA (80/20) blends as a function of VA content is shown in Figure 3. Phase separation occurs between the PHBM and EVA when VA content is less than 70 wt%, indicating an immiscible feature. Since the vinyl acetate segments are miscible with the PHBM matrix, [19] the interfacial properties of the PHBM/EVA blends are improved with an increase in VA content. The particle size of the EVA40 in the blend is relatively large ($\sim 3 \mu\text{m}$) being ascribed to a high interfacial tension. The EVA particle size is decreased to $\sim 1 \mu\text{m}$ with increasing the VA content to 70 wt% (Figure 3a–3c). On the other hand, no phase separation is observed in the PLA/EVA90 blend (Figure 3d) as they are miscible. It has to be remarked that heterogeneities and oriented pattern on the PHBM/EVA90 surface (Figure 3d) are caused in sample preparation (microtome) process. The single-phase morphology of the PHBM/EVA90 blend is further confirmed by TEM characterization as shown by the inset in Figure 3d.

3.2. Effect of VA content on the mechanical properties of PHBM/EVA blends

Miscibility and morphology are crucial to mechanical properties of a polymer blend. Tensile properties of the PHBM/EVA (80/20, wt/wt) blends as a function of VA content are investigated and shown in Figure 4. All the blends show yielding behavior during tensile test. The maximum tensile strength (σ_{m-t}) of the blends increases gradually with the VA content. The highest σ_{m-t} (30 MPa) and elongation at break ($\varepsilon_b = 150\%$) are obtained at the VA content of 90 wt%. The E -modulus of the blends varies between 600 and 800 MPa when the VA content increases from 40 to 90 wt%, as shown in Figure 4b. Neat PHBM is rigid with σ_{m-t} and ε_b of 36 MPa and 5.6%

respectively (see Figure 5), thus the ductility of PHBM was improved by addition of 20 wt% EVA.

3.3. Mechanical properties of PHBM/EVA90 blends

EVA90 is the most promising among the studied EVA grades in improving mechanical properties of PHBM (Figure 4), therefore the mechanical behavior of the PHBM/EVA90 blends are investigated in detail, as shown in Figure 5.

The stress-strain curves of the PHBM/EVA90 blends are shown in Figure 5a. EVA90 shows typical stress-strain behavior of an elastomer. In contrast, PHBM is brittle with high tensile stress and low elongation at break. It fractures without yielding (Figure 5a curve 1). The PHBM/EVA90 (80/20, wt/wt) shows strong strain-softening followed by a weak strain-hardening. Consequently this blend breaks at relatively low elongation, as shown in Figure 5a curve 2. Strain-softening is an indication of strain localization. If the strain cannot be delocalized brittle fracture would occur. It is known that strain can be delocalized via strain-hardening resulting in tough materials [21]. The strain-softening behavior becomes less pronounced with increasing the EVA90 content up to 70 wt%, while the strain-hardening becomes more pronounced. As a consequence, the blends with high EVA90 content behave as thermoplastic elastomers (TPE) or thermoplastic vulcanizates (TPV) [22]. Figure 5b shows the yield stress (σ_y) and yield strain (ε_y) of the PHBM/EVA90 blends. The σ_y decreases monotonically with increasing EVA90 content accompanied by an increase in ε_y indicating an enhanced ductility. The σ_{m-t} and ε_b of the blends (Figure 5c) show similar trends as the σ_y and ε_y respectively. Remarkably, the ε_b of the PHBM is

Figure 4. Tensile properties of the PHBM/EVA (80/20, wt/wt) blends as a function of VA contents. (a) maximum tensile strength and elongation at break and (b) E -modulus.

Figure 5. Mechanical behaviour of the PHBM/EVA90 blends as a function of EVA90 contents. (a) stress-strain curves, (b) yield stress and yield strain, (c) maximum tensile strength and elongation at break and (d) *E*-modulus. The stress-strain curves of 1–6 in Figure 5a correspond to the PHBM/EVA90 blends with the EVA90 content of 0, 20, 30, 50, 70 and 100 wt% respectively, and the initial stage of the stress-strain curves is inset in Figure 5a to clarify the yielding behavior of the samples.

increased by a factor of more than 140 after addition of 30–50 wt% of the EVA90. Meanwhile, the σ_{m-t} is much higher than the σ_y , notably at high EVA90 content because of the pronounced strain-hardening. In addition, *E*-modulus of the blends decreases with increasing the EVA90 content, as shown in Figure 5d. These results display elastic behavior of the PHBM/EVA90 blends.

3.4. Strain-recovery behavior of PHBM/EVA90 blends

The PHBM/EVA90 blends show high and fast strain-recovery within a short time (>60% within 4 min), as demonstrated in Figure 6. The strain-recovery feature remains in the repeating cycles. These results indicate good elasticity and rubbery characters of the blends. Meantime, the PHBM/EVA90 blends exhibit notable stress-strain hysteresis which is a characteristic feature of thermoplastic elastomers [23]. The lower content of the EVA90 the more remarkable hysteresis. It is also noticed that the hysteresis mainly occurs in the first hysteresis stress-strain cycle since

the second and third cycles are close to each other (the 3rd cycle is not shown here to make the curves more readable). EVA90 shows very similar strain-recovery behavior as the blends (Figure 6d). Hence, the existence of EVA90 might be one of the key reasons for the elastic behavior of the PHBM/EVA90 blends.

3.5. Mechanism of the thermoplastic elasticity of PHBM/EVA90 blends

Heterogeneities are needed for toughness of polymers while crosslink is required for elasticity. As discussed above, the PHBM/EVA90 blends show typical thermoplastic elasticity. However, neither heterogeneities nor chemical crosslinks exist in the blends. It thus would be of interest to reveal the mechanism of the thermoplastic elasticity of the blends.

A typical route to make TPE is by blending a plastic with an immiscible rubber in combination with dynamic crosslinking. [24–26] In such process the rubber phase is crosslinked and re-dispersed in the

Figure 6. Hysteresis stress-strain curves of the PHBM/EVA90 blends as a function of EVA90 contents: (a) 30 wt%, (b) 50 wt%, (c) 70 wt% and (d) 100 wt%. The 1st and 2nd cycles are indicated by Arabic numerals in the figures.

plastic phase. The re-dispersed rubber phase interconnects leading to good elastic properties and the properties are affected by rubber particle size, e.g. TPE (or TPV) from poly(propylene)/ethylene-propylene-diene rubber blends [22]. The other route to prepare TPE is by making block copolymers containing both soft and hard segments, e.g. thermoplastic poly(urethane) (TPU) and styrene-*b*-butadiene-*b*-styrene copolymers (SBS) [27, 28].

PHBM is a brittle semi-crystalline thermoplastic. The brittleness of PHBM is ascribed to large spherulites and cracks in the spherulites [5]. Therefore, the crystallization behavior (e.g. morphology and crystallinity) is important to its mechanical properties. In this study, the crystallization of PHBM in the blends was complete since no cold crystallization peaks were detected from the first heating DSC curves, as shown in Figure 7. The crystallinity (X_c) of PHBM is around 38% in the samples (Figure 8) calculated via equation $X_c = \Delta H_m / (\Delta H_0 \cdot W) \cdot 100\%$, where ΔH_0 is the melt enthalpy of 100% crystalline PHB (146.6 J/g) [29], ΔH_m is the measured melt

enthalpy of PHBM in the blends, W is the weight fraction of the PHBM in the blends. Although the X_c of PHBM was similar in different samples, the crystallization kinetics, crystal morphology and the X_c of the blends (obtained via equation $X_c = \Delta H_m / \Delta H_0 \cdot 100\%$) show strong dependence on the compositions.

Figure 7. The first heating DSC curves of the PHBM/EVA90 blends as a function of EVA90 contents: (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, (d) 30 wt%, (e) 50 wt%, (f) 70 wt% and (g) 100 wt%

Figure 8. Crystallinity (X_c) of the PHBM and the PHBM/EVA90 blends and spherulite growth rate (G) of the PHBM as a function of EVA90 contents. The G presented in Figure 8 was measured at 90°C while it shows similar trend at other temperatures (not shown here).

It was reported that crystallization kinetics of PHB were slowed down by addition of miscible PVAc. [19]. Similar behavior was observed in the PHBM/EVA90 blends e.g., the spherulite growth rate (G) of the PHBM decreases with increasing the EVA90 content, as shown in Figure 8. As a result, the spherulite morphology of the PHBM/EVA90 blends was improved by addition of the EVA90, which was studied by using polarized optical microscope (POM), as shown in Figure 9.

Large spherulites ($\sim 150 \mu\text{m}$) with cracks are observed in neat PHBM (Figure 9a) resulting in brittleness of the PHBM. The spherulite size was reduced to 50–100 μm after addition of 10–20 wt% of the EVA90, leading to a notable improvement in the toughness. Due to the decrease in G and the presence of nucleating agents, a large number of spherulites with sub- μm dimensions are uniformly dispersed in the PHBM/EVA90 blends when the EVA90 content is higher than 30 wt% (Figures 9d, 9e and 9f). Such morphology is associated with the above discussed thermoplastic elastomeric properties. The EVA90 molecules are diluted in the PHBM matrix when the EVA90 content is lower than 20 wt%, whereas the EVA90 molecules may inter-entangle at high content ($>30 \text{ wt\%}$) in the blends. Since the EVA90 is amorphous and rubbery (Figure 9g and Figure 5a), it exists as random coil in the amorphous region of the blends, i.e. between PHBM lamellae and between spherulites. The lamellae and fine spherulites play a role of physical crosslink points of the amorphous PHBM and the rubbery EVA90 molecules resulting in a thermoreversible

network. The network is schematically illustrated in Figure 10a. The stress under deformation can be delocalized by stretching the random coils and the physical network (Figure 10b), thus toughness and ductility of the blends are obtained. The deformation can be recovered to a high degree when the stress is removed because random coil is the favorable state of the rubbery molecules, as illustrated in Figure 10a–10b. Consequently, this special structure results in high elasticity of the PHBM/EVA90 blends. Another advantage is that the blends are easily processable after melting and show elastic behavior after crystallization, as illustrated in Figure 10a–10c.

4. Conclusions

The properties of poly(hydroxyalkanoate)s (PHBM, Metabolix) were modified by poly(ethylene-co-vinyl acetate) (EVA) using a melt-blending technique. The miscibility between the PHBM and EVA were studied via thermal analysis (DMA and DSC) and microscopy (SEM and TEM). The PHBM is immiscible with EVA at VA content lower than 70 wt%, while is miscible with EVA90 which contains 90 wt% of VA. The effect of VA content on the mechanical properties of the PHBM/EVA (80/20, wt/wt) blends was studied. The PHBM/EVA90 (80/20, wt/wt) blend shows higher maximum tensile strength (σ_{m-t}) and larger elongation at break (ϵ_b) than the others. PHBM is brittle and stiff with high σ_{m-t} and low ϵ_b . It is toughened by 20 wt% of the EVA90 showing notable stress yielding and high elongation at break. Interestingly, thermoplastic elastomeric behavior of the PHBM/EVA90 blends was achieved when the EVA90 content is higher than 30 wt%, i.e., high ϵ_b ($>800\%$), good strain-recovery and moderate E -modulus ($<500 \text{ MPa}$). The thermoplastic elastomeric properties of the PHBM/EVA90 blends are associated with their structures. Crystallization of the PHBM occurred in the PHBM/EVA90 blends upon cooling. Since the EVA90 is thermodynamically miscible with the PHBM it exists among the PHBM crystals (lamellae and spherulites). Moreover the spherulite growth rate of PHBM is reduced in the presence of EVA90 which results in small spherulite size but large in numbers. Consequently the PHBM crystals, e.g. the large number of fine spherulites act as crosslink points leading to a physical network in the blends. The physical network and elastic EVA90 molecules are considered to be responsible for the thermoplastic elastomeric prop-

Figure 9. Polarized optical microscope images (scale bar = 50 μm , same magnification) of the PHBM/EVA90 blends as a function of EVA90 contents: (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, (d) 30 wt%, (e) 50 wt%, (f) 70 wt% and (g) 100 wt%. The images were taken from compression molded samples. The average spherulite size is shown on the top left of each image.

Figure 10. Schematic illustration of micro-structures of the PHBM/EVA90 blends in different states: (a) solid static state, (b) stretched state and (c) melt state. (a)–(b) shows the elastic behavior while (a)–(c) shows the thermoplastic behavior.

erties. Therefore, a new class of partially bio-based thermoplastic elastomers (bio-TPE) is designed and prepared which has potential application in substitution of conventional TPE materials.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (51303067, 51173072) and the Natural Science Foundation of Jiangsu Province (BK20130147). The authors acknowledge P. Schmit and A.B. Spoelstra from Eindhoven University of Technology in the Netherlands for valuable discussions on the morphology characterization and acknowledge Lanxess Chemical Co., Ltd. for kindly providing EVA (Levapren® EVM) materials.

References

- [1] Saito Y., Doi Y.: Microbial synthesis and properties of poly(3-hydroxybutyrate-co-4-hydroxybutyrate) in *Comamonas acidovorans*. *International Journal of Biological Macromolecules*, **16**, 99–104 (1994). DOI: [10.1016/0141-8130\(94\)90022-1](https://doi.org/10.1016/0141-8130(94)90022-1)
- [2] Rodríguez-Contreras A., Koller M., Dias M. M. D.: Calafell-Monfort M., Braunegg G., Marqués-Calvo M. S.: High production of poly(3-hydroxybutyrate) from a wild *Bacillus megaterium* Bolivian strain. *Journal of Applied Microbiology*, **114**, 1378–1387 (2013). DOI: [10.1111/jam.12151](https://doi.org/10.1111/jam.12151)
- [3] Lemoigne M.: Assay of poly-β-hydroxybutyric acid. *Bulletin de la Societe de Chimie Biologique*, **8**, 770–782 (1926).
- [4] Sudesh K., Abe H., Doi Y.: Synthesis, structure and properties of polyhydroxyalkanoates: Biological polyesters. *Progress in Polymer Science*, **25**, 1503–1555 (2000). DOI: [10.1016/S0079-6700\(00\)00035-6](https://doi.org/10.1016/S0079-6700(00)00035-6)

- [5] Hobbs J. K., McMaster T. J., Miles M. J., Barham P. J.: Cracking in spherulites of poly(hydroxybutyrate). *Polymer*, **37**, 3241–3246 (1996). DOI: [10.1016/0032-3861\(96\)88468-0](https://doi.org/10.1016/0032-3861(96)88468-0)
- [6] Ma P., Hristova-Bogaerds D. G., Lemstra P. J., Zhang Y., Wang S.: Toughening of PHBV/PBS and PHB/PBS blends via *in situ* compatibilization using dicumyl peroxide as a free-radical grafting initiator. *Macromolecular Materials and Engineering*, **297**, 402–410 (2012). DOI: [10.1002/mame.201100224](https://doi.org/10.1002/mame.201100224)
- [7] Tanadchangsang N., Yu J.: Miscibility of natural polyhydroxyalkanoate blend with controllable material properties. *Journal of Applied Polymer Science*, **129**, 2004–2016 (2013). DOI: [10.1002/app.38906](https://doi.org/10.1002/app.38906)
- [8] Madden L. A., Anderson A. J., Asrar J.: Synthesis and characterization of poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) polymer mixtures produced in high-density fed-batch cultures of *Ralstonia eutropha* (*Alcaligenes eutrophus*). *Macromolecules*, **31**, 5660–5667 (1998). DOI: [10.1021/ma980606w](https://doi.org/10.1021/ma980606w)
- [9] Doi Y., Kitamura S., Abe H.: Microbial synthesis and characterization of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate). *Macromolecules*, **28**, 4822–4828 (1995). DOI: [10.1021/ma00118a007](https://doi.org/10.1021/ma00118a007)
- [10] Parulekar Y., Mohanty A. K.: Biodegradable toughened polymers from renewable resources: Blends of polyhydroxybutyrate with epoxidized natural rubber and maleated polybutadiene. *Green Chemistry*, **8**, 206–213 (2006). DOI: [10.1039/B508213G](https://doi.org/10.1039/B508213G)
- [11] Basnett P., Ching K. Y., Stolz M., Knowles J. C., Boccacini A. R., Smith C., Locke I. C., Keshavarz T., Roy I.: Novel poly(3-hydroxyoctanoate)/poly(3-hydroxybutyrate) blends for medical applications. *Reactive and Functional Polymers*, **73**, 1340–1348 (2013). DOI: [10.1016/j.reactfunctpolym.2013.03.019](https://doi.org/10.1016/j.reactfunctpolym.2013.03.019)
- [12] de O. Patrício P. S., Pereira F. V., dos Santos M. C., de Souza P. P., Roa J. P. B., Orefice R. L.: Increasing the elongation at break of polyhydroxybutyrate biopolymer: Effect of cellulose nanowhiskers on mechanical and thermal properties. *Journal of Applied Polymer Science*, **127**, 3613–3621 (2013). DOI: [10.1002/app.37811](https://doi.org/10.1002/app.37811)
- [13] Fei B., Chen C., Wu H., Peng S., Wang X., Dong L., Xin J. H.: Modified poly(3-hydroxybutyrate-co-3-hydroxyvalerate) using hydrogen bonding monomers. *Polymer*, **45**, 6275–6284 (2004). DOI: [10.1016/j.polymer.2004.07.008](https://doi.org/10.1016/j.polymer.2004.07.008)
- [14] Dong W., Ma P., Wang S., Chen M., Cai X., Zhang Y.: Effect of partial crosslinking on morphology and properties of the poly(β-hydroxybutyrate)/poly(D,L-lactic acid) blends. *Polymer Degradation and Stability*, **98**, 1549–1555 (2013). DOI: [10.1016/j.polymdegradstab.2013.06.033](https://doi.org/10.1016/j.polymdegradstab.2013.06.033)

- [15] de Koning G. J. M., Lemstra P. J.: Crystallization phenomena in bacterial poly[(R)-3-hydroxybutyrate]: 2. Embrittlement and rejuvenation. *Polymer*, **34**, 4089–4094 (1993).
DOI: [10.1016/0032-3861\(93\)90671-V](https://doi.org/10.1016/0032-3861(93)90671-V)
- [16] Calvão P. S., Chenal J.-M., Gauthier C., Demarquette N. R., dos Santos A. M., Cavaille J. Y.: Influence of the rubbery phase on the crystallinity and thermomechanical properties of poly(3-hydroxybutyrate)/elastomer blends. *Polymer International*, **59**, 851–858 (2010).
DOI: [10.1002/pi.2799](https://doi.org/10.1002/pi.2799)
- [17] Chiu H.-J.: Miscibility and crystallization kinetics of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/poly(methyl methacrylate) blends. *Journal of Applied Polymer Science*, **91**, 3595–3603 (2004).
DOI: [10.1002/app.13592](https://doi.org/10.1002/app.13592)
- [18] Parra D. F., Fusaro J., Gaboardi F., Rosa D. S.: Influence of poly(ethylene glycol) on the thermal, mechanical, morphological, physical–chemical and biodegradation properties of poly(3-hydroxybutyrate). *Polymer Degradation and Stability*, **91**, 1954–1959 (2006).
DOI: [10.1016/j.polymdegradstab.2006.02.008](https://doi.org/10.1016/j.polymdegradstab.2006.02.008)
- [19] Hay J. N., Sharma L.: Crystallisation of poly(3-hydroxybutyrate)/polyvinyl acetate blends. *Polymer*, **41**, 5749–5757 (2000).
DOI: [10.1016/S0032-3861\(99\)00807-1](https://doi.org/10.1016/S0032-3861(99)00807-1)
- [20] He M. J., Chen X. W., Dong X. X.: *Polymer physics* (in Chinese). Fu Dan University Press, Shanghai (2005).
- [21] Meijer H. E. H., Govaert L. E.: Mechanical performance of polymer systems: The relation between structure and properties. *Progress in Polymer Science*, **30**, 915–938 (2005).
DOI: [10.1016/j.progpolymsci.2005.06.009](https://doi.org/10.1016/j.progpolymsci.2005.06.009)
- [22] L'Abée R. M. A., van Duin M., Spoelstra A. B., Goossens J. G. P.: The rubber particle size to control the properties-processing balance of thermoplastic/cross-linked elastomer blends. *Soft Matter*, **6**, 1758–1768 (2010).
DOI: [10.1039/b913458a](https://doi.org/10.1039/b913458a)
- [23] Wiyatno W., Fuller G. G., Pople J. A., Gast A. P., Chen Z.-R., Waymouth R. M., Myers C. L.: Component stress–strain behavior and small-angle neutron scattering investigation of stereoblock elastomeric polypropylene. *Macromolecules*, **36**, 1178–1187 (2003).
DOI: [10.1021/ma020477q](https://doi.org/10.1021/ma020477q)
- [24] Kakroodi A. R., Rodrigue D.: Degradation behavior of maleated polyethylene/ground tire rubber thermoplastic elastomers with and without stabilizers. *Polymer Degradation and Stability*, **98**, 2184–2192 (2013).
DOI: [10.1016/j.polymdegradstab.2013.08.017](https://doi.org/10.1016/j.polymdegradstab.2013.08.017)
- [25] Wu W., Wan C., Zhang Y.: Morphology and mechanical properties of ethylene-vinyl acetate rubber/polyamide thermoplastic elastomers. *Journal of Applied Polymer Science*, **130**, 338–344 (2013).
DOI: [10.1002/app.39046](https://doi.org/10.1002/app.39046)
- [26] Zhou Z., Zhang X., Zhang W., Li J., Lu C.: Microstructure and properties of solvent-resistant fluorine-contained thermoplastic vulcanizates prepared through dynamic vulcanization. *Materials and Design*, **51**, 658–664 (2013).
DOI: [10.1016/j.matdes.2013.04.070](https://doi.org/10.1016/j.matdes.2013.04.070)
- [27] Hrdlička Z., Kuta A., Poręba R., Špírková M.: Polycarbonate-based polyurethane elastomers: Temperature-dependence of tensile properties. *Chemical Papers*, **68**, 233–238 (2014).
DOI: [10.2478/s11696-013-0439-0](https://doi.org/10.2478/s11696-013-0439-0)
- [28] Huy T. A., Adhikari R., Michler G. H.: Deformation behavior of styrene-*block*-butadiene-*block*-styrene tri-block copolymers having different morphologies. *Polymer*, **44**, 1247–1257 (2003).
DOI: [10.1016/S0032-3861\(02\)00548-7](https://doi.org/10.1016/S0032-3861(02)00548-7)
- [29] Barham P. J., Keller A., Otun E. L., Holmes P. A.: Crystallization and morphology of a bacterial thermoplastic: Poly-3-hydroxybutyrate. *Journal of Materials Science*, **19**, 2781–2794 (1984).
DOI: [10.1007/BF01026954](https://doi.org/10.1007/BF01026954)