Crystallization kinetics and miscibility of blends of polyhydroxybutyrate (PHB) with ethylene vinyl acetate copolymers (EVA)

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Abstract: A series of ethylene vinyl acetate random copolymer EVA, with vinyl acetate (VA) varied from 9 to 91m%, was investigated by differential scanning calorimetry DSC and polarized optical microscopy. Biodegradable polymer blends of polyhydroxybutyrate PHB and EVA, having VA in EVA in range from 40m% till 91m%, were prepared by film casting from a chloroform solution. The miscibility and crystallization behavior of these blends were investigated. The isothermal crystallization behaviors of PHB and PHB/EVA blends are discussed in terms of the half time of crystallization $t_{1/2}$. Experimental results indicated that blends of PHB/ EVA91 are completely miscible blend in the entire (0 to 100 m%) compositional ranges. Blends PHB/ EVA, for VA varied from 40 till 70 m% are immiscible as evidenced by the existence of unchanged composition independent glass transition temperatures (T_g), crystallization and melting behavior. The isothermal crystallization of PHB blends was investigated from room temperature till 130 °C. 80 °C was found to be the best temperature for comparison of different blends. At 80 °C $t_{1/2}$ strongly depends on the content of VA in PHB/EVA blend, mainly due to differences in miscibility as well as due to differences in segmental mobility as identified by differences in glass transition temperature. Since both components in PHB/EVA80, pure PHB and pure EVA80, have glass transition temperatures close to 0 °C, it is difficult to decide its miscibility from T_g. However from the strong dependence of the value of crystallization half time $t_{1/2}$ of PHB/EVA80 on blend composition, it was possible to reasonably infer that PHB/EVA80 is partially miscible.

Introduction

Polyhydroxybutyrate (PHB) produced by microorganisms as carbon and energy reserves has attracted much interest due to its biodegradability and biocompatibility [1, 2]. PHB is a highly crystalline thermoplastic polymer with a relatively high melting temperature in the range of 170 °C–180 °C and its glass transition temperature is around 0 °C [3]. Although a number of works have been reported on the biosyntheses, physical properties and biodegradation behavior of PHB, its inherent

brittleness [4-9], narrow processing window [10] as well as high production cost limit their more versatile practical applications. For this reason, two approaches have been extensively studied to improve the physical properties of PHB. One approach is the microbial synthesis of copolymer containing hydroxyalkanoate monomeric units other than the R-PHB unit [11]. The second approach is the blending of PHB with other polymers [12, 13]. A number of works have been published in this field; the blend partners of PHB include non biodegradable polymers such as polyvinyl acetate (PVAC) [14-16], polymethacrylate (PMA) [17 -18], as well as biodegradable polymers such as polyethylene oxide (PEO) [19-20] , polyvinyl alcohol PVA [21] , poly ε-caprolactone (PCL), polysaccharids, etc. [12, 13].

Thermal, physical properties and the rate of biodegradability of the blends are significantly affected by the nature of the blend partner of PHB, like biodegradability, and or miscibility with PHB. It was reported that for miscible blends [12,13,14-16,18, 22-29] like PHB/PVAC [14-16], PHB/chemo-synthetic R, S –PHB-OH [22-23], PHB/(poly(vinyl acetate-co- vinyl alcohol), where vinyl alcohol content 9m% [24], poly(ethylene-co-vinyl acetate) (EVA) where m% of VA is 85 [25] overall crystallization rate of PHB, and spherulitic growth rate decrease with increasing content of another partner in PHB blends. However for immiscible PHB blends [14, 24, 25, 30-33] no change in radial spherultic growth rate of PHB in PHB blends was observed. But the overall crystallization rate of PHB decreases with increasing content of the blend partner. Authors attributed this result to; (i) the presence of the second partner has a negative effect on the primary nucleation of PHB, (ii) the presence of the second partner increases the energy required to transport macromolecules of PHB in the melt towards the crystal growth front.

The requirements for mechanical property improvement by blending are the following (i) glass transition temperatures of these blends are lower than room temperature, (ii) the PHB content is less than 60m% (crystallinity Xc <0.4), and (iii) high molecular mass of the blend partner [34]. Since the glass transition temperature of commercial high molecular mass ethylene vinyl acetate copolymer EVA varies from -30 ^{o}C till 38 ^{o}C corresponding to the ratio of ethylene to vinyl acetate [35- 37], it is expected, and according to [34] the case that EVA can be a good partner to improve the mechanical properties of PHB without an additional plasticizer. It is well known that EVA properties can change with increasing vinyl acetate content from semicrystalline thermoplastic to elastomeric materials and finally to thermoplastic amorphous materials [36, 37].

In the present study, the goal is to investigate systematically the influence of molecular structure (such as the vinyl content) of a non-crystallizable EVA copolymer on the melt miscibility, phase structure, morphology, thermal and crystallization behavior of blends based on poly(hydroxybutyrate) (PHB).

Results and discussion

Ethylene vinyl acetate copolymers

In order to get precise information about the glass transition temperature, and the crystallization and melting behavior of the vinyl acetate copolymers (EVA), where vinyl acetate content (VA) varies from 9m% (EVA9) to 91m% (EVA91) DSC scans were done from -50 ^{o}C till 130 ^{o}C, where the heating and cooling rates were 20

K/min. The glass transition temperature T_g was evaluated from the second DSC heating run as the half step temperature (see Figure 1), and is tabulated in Table 1.
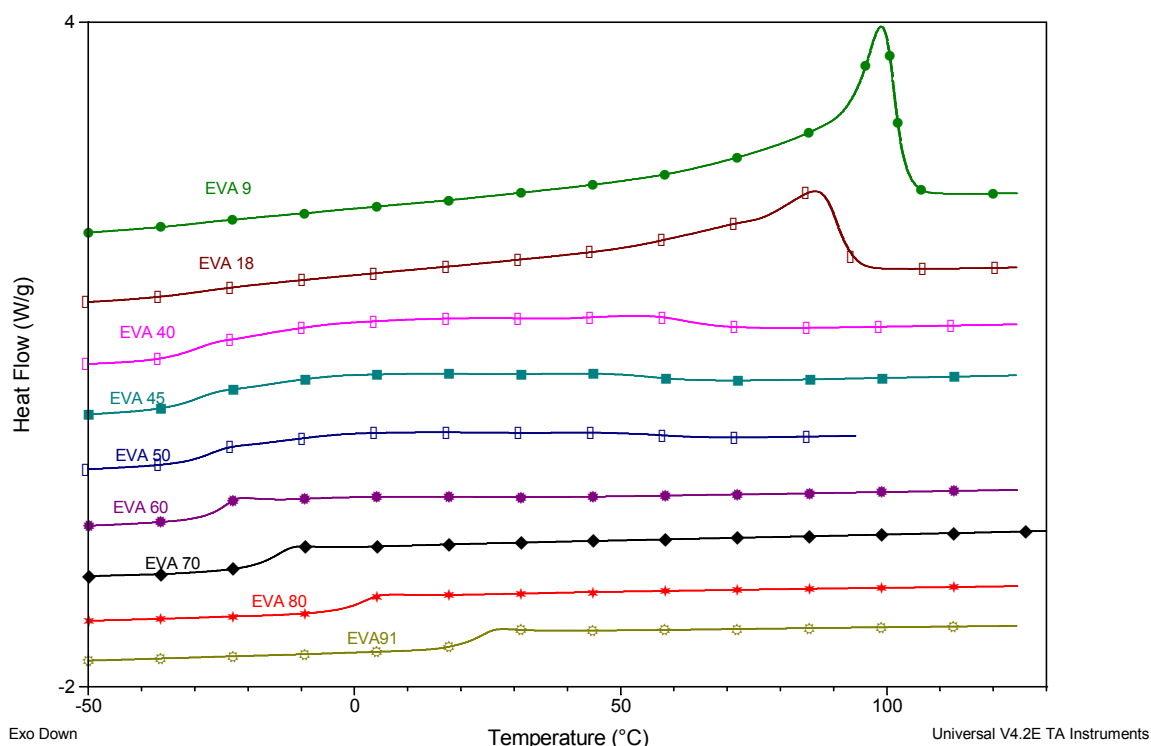
Fig. 1. DSC second heating scan of pure ethylene vinyl acetate copolymers (EVA) where VA m% content changes from 9m% to 91m% as indicated in the figure. Curves are shifted vertically for clarity.

The variation of glass transition temperature as a function of m% of vinyl acetate, VA%, in EVA is represented in Figure 2. As expected, with increasing concentration of vinyl acetate in EVA the glass transition shifts to higher values. For example, the glass transition temperature of EVA40 is -30 ^{o}C, however for EVA91 it is 19 ^{o}C. In the range from 40% VA till 60% VA the glass transition temperature is nearly constant (See Figures 1 and 2). This means the amount of ethylene with respect to vinyl acetate in the amorphous phase is constant in this range. The remaining amount of ethylene is accumulated in the crystalline phase.

A strong endothermic melting peak is observed for EVA9, EVA18 with $T_{m\ max}$ 92 ^{o}C and 87 ^{o}C, respectively. However, for EVA40 till EVA60 only weak broad melting peaks are observed in the temperature range from 0 °C till 50 ^{o}C. The area under the melting peak was evaluated. X_c is estimated by dividing the area under the melting peak by 293 J/g, ΔH_m for 100% crystalline PE at the equilibrium melting temperature. Therefore the crystallinity for the low melting temperature copolymers is slightly underestimated. The values of X_c are tabulated in Table 1, and plotted in Figure 2.

Tab. 1. DSC scan results.

Materials		T_g/°C	T_m/°C	X_c
Pure PHB		0-3 °C	172	0.63
	Pure EVA	VA m% content		
EVA9	9	-23 °C	92 °C	0.30
EVA 18	18	-28 °C	87 °C	0.24
EVA 40	40	-30 °C	18 °C	0.11
EVA 45	45	-30 °C	nd	0.78
EVA50	50	-30 °C	nd	0.59
EVA60	60	-28 °C	nd	0
EVA70	70	-17 °C	nd	0
EVA80	80	-1 °C	nd	0
EVA91	90	+19 °C	nd	0

nd - not detected

The presence of more than 60% VA completely hindered the crystallization of the ethylene unit in the copolymers (see Figures 1 and 2) and Table 1), i.e above EVA60 the copolymers are completely amorphous. Increasing VA content causes a decrease of melting temperature and crystallinity in EVA. A similar trend was observed in [41]. Su et al. [42] reported that the copolymers become completely amorphous when the VA content exceeds 50m%.
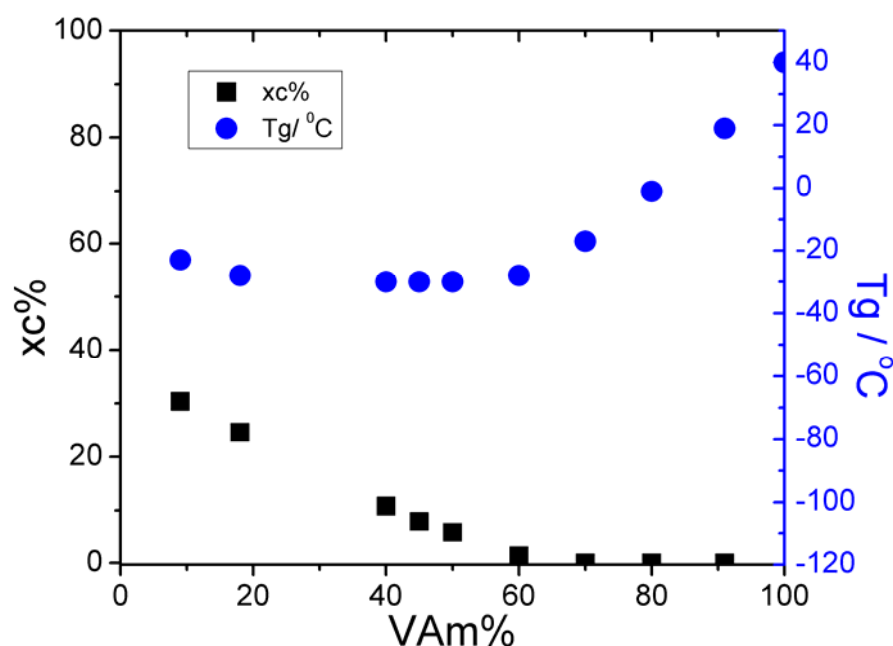

Fig. 2. Glass transition temperature T_g, and percent of crystallinity X_c as a function of vinyl acetate content in ethylene vinyl acetate copolymers.

In order to overcome the brittleness of PHB an approach is to blend 50 m% of PHB with a rubbery amorphous high molecular weight polymer [34]. Since crystallization,

thermal properties, and miscibility of the blends are significantly affected by the nature of the blend partner of PHB [12, 13, 25], it was decided to blend PHB with EVA copolymers in the range from VA40 till V91.

Thermal behavior of PHB-EVA copolymer

In order to study the thermal behavior of PHB/EVA blends, DSC scans were performed. DSC cycle runs were done for PHB/EVA blends with heating and cooling rate 20 K/min in the temperature range from -50 ^{o}C to 200 ^{o}C. The first heating scan of cast films ends at 200 ^{o}C in order to remove all thermal history of the samples. Figure 3 shows DSC cooling curves of pure PHB, and blends of 50m%PHB/50m%EVA at cooling rate 20 K/min.
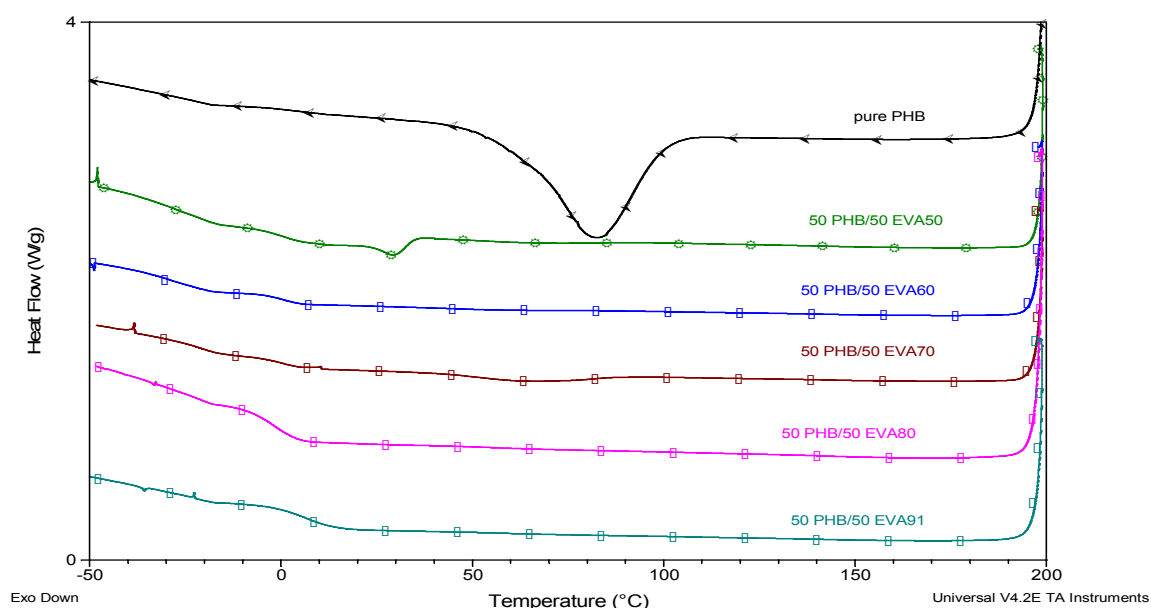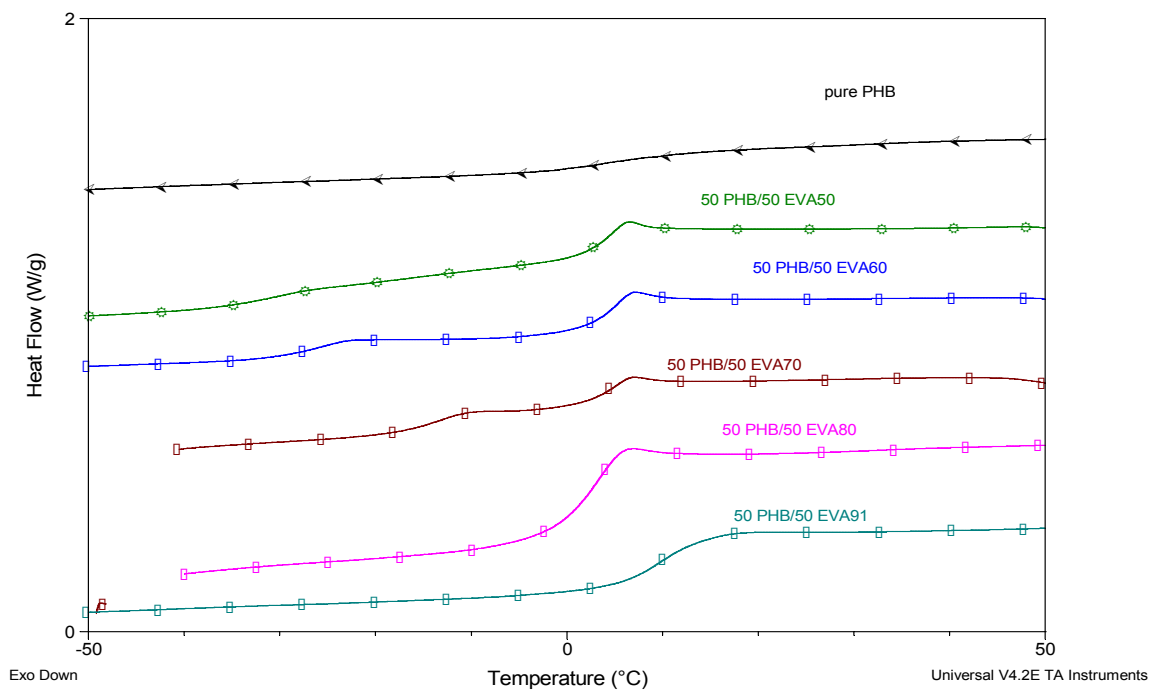

Fig. 3. DSC cooling curve of pure PHB, blend 50 m%PHB/50m%EVA, where cooling rate is 20 K /min from 200 ^{o}C to -50 ^{o}C. Curves are vertically shifted

The maximum of the exothermic crystallization peak of pure PHB occurs at 80 ^{o}C. From Figure 3 it is seen that crystallization temperature shifts to lower values (from 80 ^{o}C to 64 ^{o}C) with addition of 50m% EVA70. No exothermic crystallization peaks are observed for blends of PHB with 50m% EVA 40, EVA60, EVA80, and EVA 91. The addition of 50m% of the following compositions: EVA40, EVA60, EVA80, and EVA 91 copolymer completely hindered the crystallization of PHB. These blends are completely amorphous after cooling from the molten state at 20 K/min. This behavior is known from other blends of PHB with amorphous polymers [12, 13, 16, 22, 25, 28, 29], or blends with semicrystalline polymers like PHB/PCL [31]. In [12, 13, 16, 22] this phenomenon is attributed to two reasons: (i) the dilution of the PHB chains at the crystal growth front, and (ii) the drop of the thermodynamic crystallization driving force. Another possible reason is (iii) transfer of heterogeneities from PHB to the EVA phase that retards primary nucleation in such a way that PHB crystallization is only possible upon subsequent heating (see Figure 4-a).

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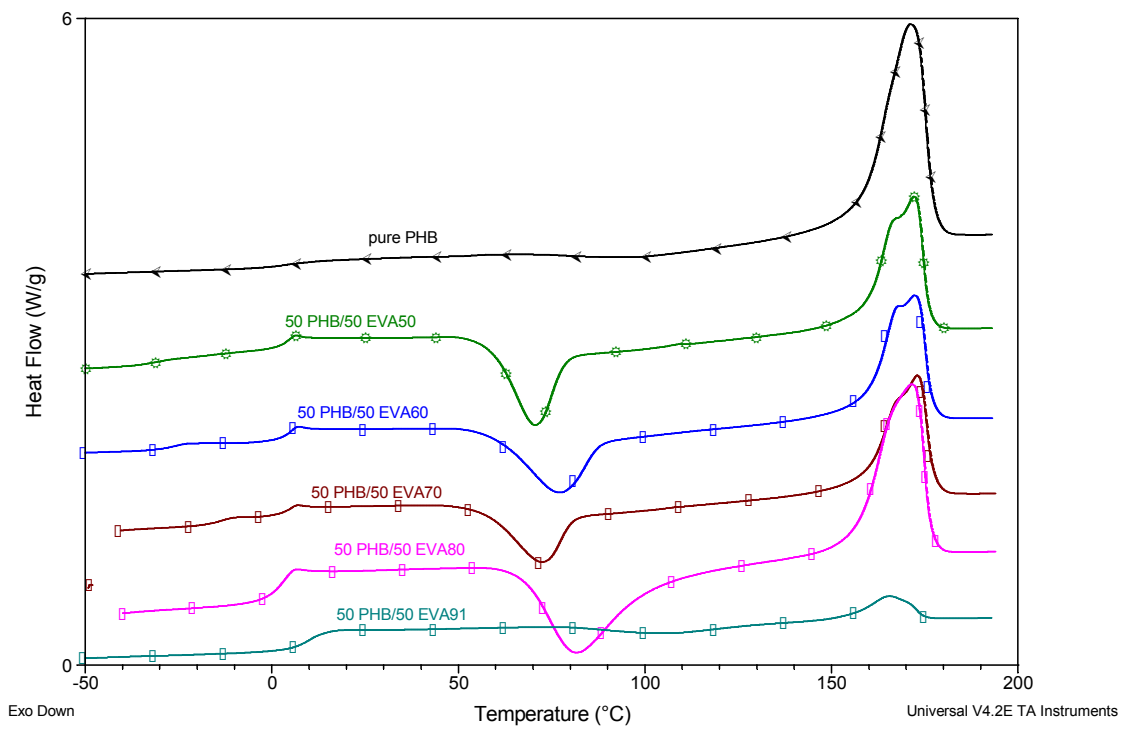
Fig. 4-a. DSC second heating curve of pure PHB, blend 50m%PHB/50m%EVA, where heating rate is 20 K/min from -50 °C till 200 °C.

Fig. 4-b. DSC second heating curve of pure PHB, blend 50m%PHB/ 50m%EVA, where heating rate is 20 K/min from -50 till 50 °C.

Figure 4-b shows second heating DSC curves for blend of 50m%PHB/50m%EVA. 50m%PHB/50m%EVA91 shows one distinct T_g at about 10 °C, which is in coincidence with that predicted by the Fox equation. It shows that the blend of 50m%PHB/50m%EVA91 is completely miscible in its amorphous state. Although 50m%PHB/50m%EVA80 has one distinct T_g at about 0 °C, it is difficult to decide its miscibility. Since the glass transition temperature of pure EVA80 is 0 °C is the same as the glass transition temperature of pure PHB. For 50m%PHB/50m%EVA40, or EVA60, or EVA70 two distinct T_gs are observed; the lower one is almost close to that of the neat EVA copolymer, while the second higher T_g corresponds to that of pure PHB at 3 °C (see Figure 4-b and Table 2). Two distinct T_gs are also observed for blends of PHB/EVA60, or EVA70, with different compositions and tabulated in Table (2).

From this it is seen that miscibility greatly depends on the content of vinyl acetate in ethylene vinyl acetate copolymers. PHB/EVA blends with VA content 40m% till 70m% are immiscible, however the blends of PHB/EVA91 are miscible. It seems that the more ethylene content in EVA copolymer, the blend becomes immiscible. This result is in a good agreement with [14, 30, 25]. It was reported that PHB is immiscible with LLDPE [30], and ethylene propylene rubber, EPR [14], and EVA70. While PHB is miscible with pure PVAC [14-16], EVA85 [25], poly(vinyl acetate-co- vinyl alcohol), where the vinyl alcohol content is 9m% [24].

Tab. 2. DSC results of PHB-EVA blends.

Material	T_c onset	T_c max	$T_c$max cold crystallization	T_m max	T_g
	Cooling scan			2nd heating scan	
PHB	101°C	83° C	98° C	171° C	
50m%PHB/50m%EVA40	nd	nd	70° C	172° C	3° C,-30° C
50m%PHB/50m%EVA50	nd	nd	68° C	172° C	3° C,-30° C
75m%PHB/25m%EVA60	89	64° C	66° C	173° C	+3° C
50m%PHB/50m%EVA60	nd	nd	77° C	173° C	+3° C,-28° C
25m%PHB/75m%EVA60	86	74° C	nd	168° C	+3° C,-28° C
75m%PHB/25m%EVA70	89	60° C	76° C	173° C	+3,° C -15° C
50m%PHB/50m%EVA70	nd	nd	73° C	173° C	+3° C,-14° C
25m%PHB/75m%EVA70	nd	nd	84° C	171° C	+1° C,-15° C
75m%PHB/25m%EVA80	nd	nd	80° C	172° C	1° C
50m%PHB/50m%EVA80	nd	nd	82° C	172° C	1° C
25m%PHB/75m%EVA80	nd	nd	105° C	168° C	1° C
75m%PHB/25m%EVA91	nd	nd	83° C	172° C	0° C
50m%PHB/50m%EVA91	nd	nd	107° C	166° C	10° C
25m%PHB/75m%EVA91	nd	nd	nd	168° C	14° C

nd - not detected

Cold crystallization for Immiscible blends

In the range of 50 $^{\circ}$C to 100 $^{\circ}$C in Figure 4-a strong exothermic cold crystallization peaks are observed, which show a maximum at (75 ± 5) $^{\circ}$C. This is due to crystallization of PHB in 50m%PHB/50m%EVA40, 60, 70, 80 blends. For 50m%PHB/50m%EVA40 till 50m%EVA80 the crystallization peaks are almost constant independent of content of VA in EVA. Its maxima are very close to that observed for pure PHB during the cooling scan. For PHB/EVA, where VA varies from 40m% till 80m% the PHB spherulites grow in the presence of a PHB melt containing EVA domains. It is known that in immiscible systems [14, 17, 30-33] such as that of PHB/EVA, during growth of PHB the EVA molecules are first preferentially segregated and then accumulated in the intra-spherulitic regions. From Figures (3 and 4-a&b) it can be concluded that the crystallization and separation processes are competing with each other for 50m%PHB/50m%EVA, VA 40 till 70. Starting from the melt, the liquid/liquid phase separation occurs before the crystallization as is evidenced by the data in Figure 3 where it can be seen that no exothermic crystallization peak is observed. Before crystallization, the systems separate in two phases, mainly constituted by the two pure components. After the crystallization, three phases are present: one crystalline PHB and two amorphous phases. A similar trend was reported for PHB/PMMA [17] and the immiscible blend of PHBV/PCL [43].

Cold crystallization for Miscible blends

However, only a small and weak cold crystallization peak is observed for 50m%PHB/50m%EVA91 in the temperature range from 80 °C to 130 °C, with a maximum at 107 °C. This is attributed to two possible reasons: (i) EVA91 has the highest glass transition temperature, 19 °C, therefore the lowest mobility of macromolecules and (ii) for PHB/EVA91 PHB spherulites grow in equilibrium with a one-phase melt. For these blends the phase structure in the solid state is characterized by the presence of a homogeneous amorphous phase situated mainly in interlamellar regions of the crystalline PHB and consisting of EVA91 molecules and uncrystallized PHB chains.

Melting behavior

An endothermic melting peak with a low temperature shoulder is observed at 173 °C for the blends of 50m%PHB/50m%EVA40 till 50m%EVA80 (see Figure 4-a). It is nearly independent of the type of EVA copolymer in the range of EVA40 till EVA80. The normalized degree of crystallinity (Xc), with respect to PHB content in the blends, was calculated by dividing the area under the melting peak by the ΔH_m value of 100% crystalline PHB (146 J/g) [3]. The degree of crystallinity of PHB, normalized for the PHB content, in the blends 50m%PHB/50m%EVA40 till EVA70 is independent on the blend composition and equals about 64%. This is another indication of immiscibility of PHB with EVA, where m%VA varied between 40m% and 80m%. A depression of the melting peak is observed for PHB/EVA91. This is an indication of the miscibility of PHB with EVA91. The degree of crystallinity of PHB/EVA91 was around 15%, indicating that the presence of EVA91 had a significant negative influence on the crystallization of PHB in the PHB/EVA91 blend.

From the above results it has been demonstrated that the crystallization behaviour of the PHB in PHB/EVA blends is greatly influenced by the addition of EVA, In order to

better understand this trend, isothermal crystallization studies were conducted on various PHB/EVA systems where the composition of the EVA component is systematically varied so as to examine the influence of different compositions on the crystallization kinetics.

Isothermal crystallization kinetics

Figure 5 shows the normalized relative crystallinity X_t, of PHB at different crystallization temperatures, namely 70°, 80°, 90°, and $100\ ^oC$.
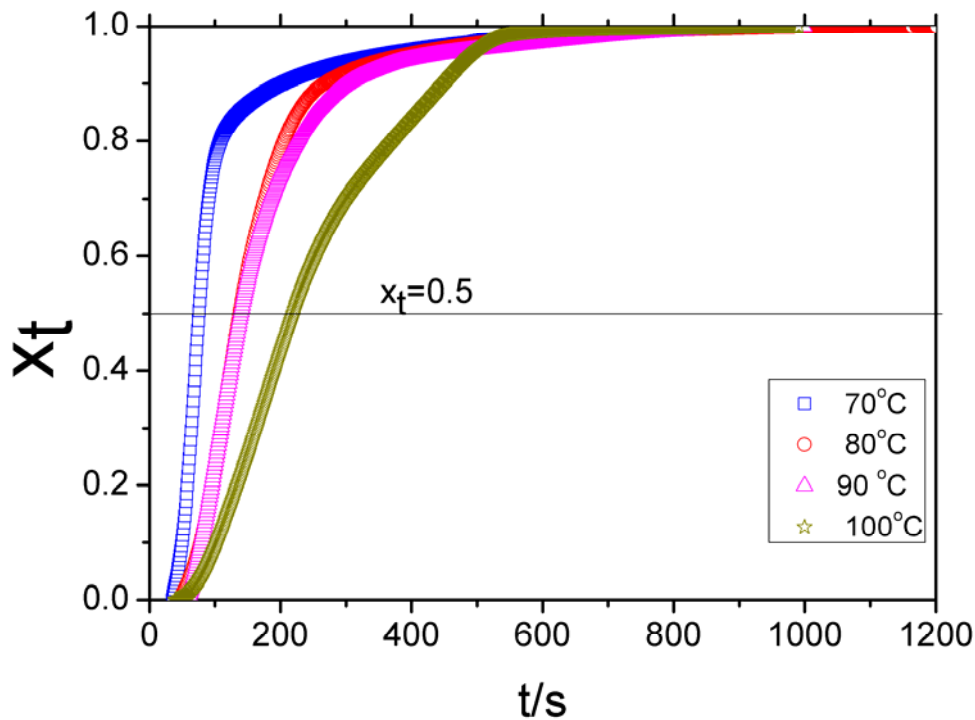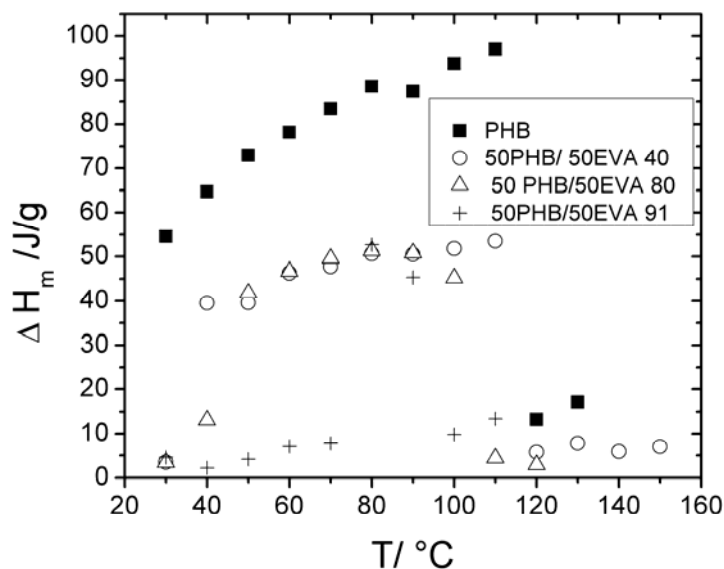
Fig. 5. Effect of crystallization temperature on the normalized relative crystallinity X_t of Pure PHB.

The normalized relative crystallinity X_t is obtained from the area of the exothermic peak of isothermal crystallization in DSC at a crystallization time t divided by the total area under the exothermic peak according Eq. (1)

$$x_t = \frac{X_c(t)}{x_c(t=\infty)} = \frac{\int_0^t (dH/dt)dt}{\int_0^\infty (dH/dt)dt} \qquad (1)$$

The numerator is the heat generated at time t and the denominator is the total heat generated during complete crystallization. It can be seen that the crystallization isotherms show the characteristic sigmoidal shape. The half-time of crystallization, $t_{1/2}$ is the time the polymer spends from the beginning of the crystallization process to the time at which 50% of relative crystallinity has been developed. With increasing crystallization temperature from 70 ^oC to 100 ^oC, $t_{1/2}$ increases from 78 s to 218 s. A similar trend was observed in the same temperature range in [44]. The crystallization

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half time is strongly dependent on both the number of nuclei and the growth rate. The time to reach complete crystallization is decreased with increasing number of nuclei and increasing growth rate [45]. Therefore, these results can be explained by taking into account the fact that the overall crystallization rate depends on the nucleation rate and on the radial growth rate of the spherulites of PHB. Braham et al. [3] reported that nucleation rate of PHB increases rapidly with increasing temperature, reaching its maximum at 80 $^{\circ}$C then decreases again. As usual the growth rate has its maximum at higher temperature. In case of PHB the maximum is at 90 $^{\circ}$C [3, 19].

In order to study the effect of ethylene vinyl acetate copolymer on the crystallization behavior of PHB in PHB/EVA blends, isothermal DSC runs at different crystallization temperatures (T_c) from 25 $^{\circ}$C till 110 $^{\circ}$C for 1h were performed. Figure 6 represents the variation of melting enthalpy (ΔH_m) of PHB, and 50m%PHB/50m%EVA blends, after 1 hour annealing as a function of crystallization temperature. It is seen that the value of the melting enthalpy greatly depends on the content of VA in EVA blends and on the crystallization temperature. It is well known that the crystallization temperature range of a crystalline polymer must lie between T_g, and T_m. When desired T_c's are located relatively near T_g, the crystallization kinetics would be controlled by the chain mobility.


Fig. 6. Melt enthalpy (ΔH_m) of 50m%PHB/50m%EVA blends , ΔH_m , as a function of crystallization temperature after 1 h annealing.

This is probably the reason for the rather low value of melting enthalpy of PHB/EVA blends in the range from room temperature till 40 $^{\circ}$C. Then the crystallization rate increases with increasing T_c. In contrast, if the desired T_c's are close to T_m the crystallization rate would be governed by the thermodynamic driving force. Therefore, as expected, the values of the melting enthalpy of the different PHB/EVA blends after one hour annealing in the range above 110 $^{\circ}$C are low. Note that at the range from 40 $^{\circ}$C till 100 $^{\circ}$C, the melting enthalpy of PHB/EVA blends are markedly higher with a maxima uniquely occurring at about 80 $^{\circ}$C. This maxima position correlates well with the maxima at which cold crystallization of PHB/EVA blends occurs as depicted in

Figure 4. For this reason the effect of EVA on the crystallization kinetics of PHB in PHB blends was studied at this temperature since direct comparisons can be made in a straight forward fashion.

It was found that the value of the melting enthalpy depends on the content of VA in EVA copolymers. Likewise, the value of the melting enthalpy for 50m%PHB/50m%EVA40 is close to that of 50m%PHB/50m%EVA80 in the whole temperature range. These results are similar to those obtained from Figure 4. However ΔH_m for 50m%PHB/50m%EVA40 is greater than ΔH_m for 50m%PHB/50m%EVA91. There are two likely reasons for this attribute (i) a reduction of molecular mobility, which directly correlates with an increase of the glass transition of the 50m%PHB/50m%EVA91 (see Figure 3, Table 2) and (ii) the miscibility of PHB/EVA91.

Figure 7 shows the variation of normalized relative crystallinity of X_t, of PHB in PHB/EVA blends during isothermal crystallization at 80 °C. It can be seen that the crystallization isotherms of PHB/EVA blends display the characteristic sigmoidal shape as pure PHB does.
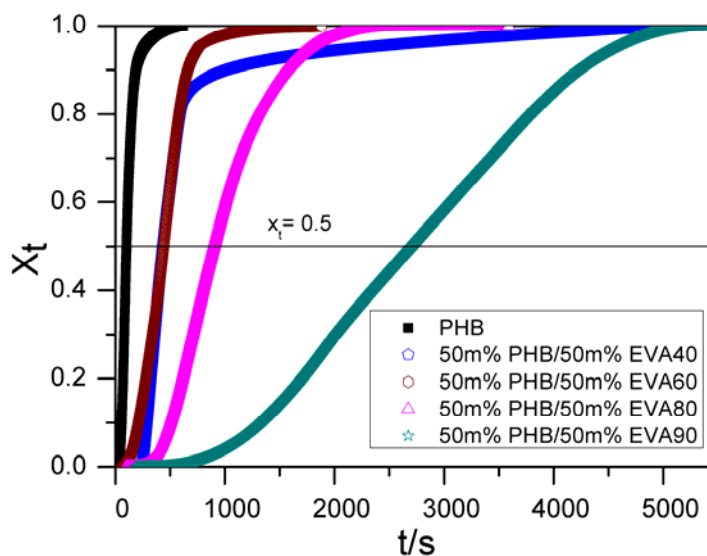

Fig. 7. Normalized relative crystallinity X_t for 50m%PHB/50m%EVA blends at crystallization temperature 80°C. The VA content in EVA is given in the legend.

From Figure 7 it is seen that with increasing VAm% in EVA in PHB/EVA blends the crystallization half time of PHB, $t_{1/2}$ increases. This is attributed to a negative effect on the primary nucleation of PHB in the presence of the EVA (see Figure 8). The number of heterogeneous primary nuclei of PHB decreases with the addition of EVA in the blends because of possible migration of heterogeneities from PHB to EVA (see Figure 8). Another possible reason of the slow-down of the crystallization rate of PHB could be a physical restriction of the growth of PHB lamellae by the EVA domains. As already reported [17, 46] the presence of a non-crystallizable material mainly influences the energy related to the transport of the macromolecules in the melt towards the growth front. In fact, during crystallization the domains of non

crystallizable material may be rejected by the growth front of the lamellae and/or they may be occluded and deformed. The presence of these domains on the growth front can markedly disturb crystallization. Energy must be dissipated to perform the occlusion, the deformation and the rejection. Such energies constitute a new energy barrier that may control the growth of the lamellae forming the spherulites [17, 46]. Similar results are reported for immiscible blends PHB/PCL [31], PHBV/PCL [43] and the immiscible blend PHBV/PBSU [33].

The value of $t_{1/2}$ is the same for 50m%PHB/50m%EVA40 and 50m%PHB/50m%EVA60 (see Table 4). These results can be correlated based on the following arguments: (i) from optical microscopy data (see Figure 8) it was found that the number of spherulites in 50m%PHB/50m%EVA60, and 50m%PHB/50m%EVA40 are the same, however these number of spherulites are considerably smaller than for that in pure PHB; (ii) both blends have the same glass transition temperature (See Table 1, 2).

| a | b | c | d |
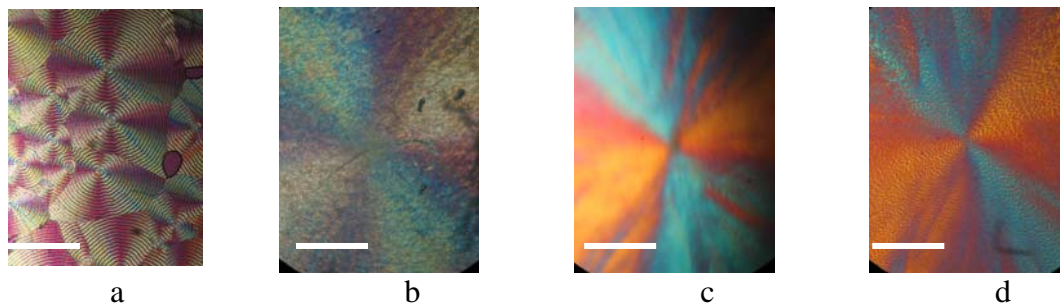
Fig. 8. Optical micrographs of a – pure PHB and 50m%PHB/50m%EVA b -EVA60, c - EVA80, and d - EVA91 blends after 1 h annealing at 80 ^{o}C. Inserted scale bar represents 200 μm.

For 50m%PHB/50m%EVA80 the $t_{1/2}$ is considerably longer than for 50m%PHB/50m%EVA40 or, 50m%PHB/50m%EVA60. This may be attributed to the fact that the glass transition temperature of 50m%PHB/50m%EVA80 is 1°C, which is larger than that of 50m%PHB/50m%EVA60 or 50m%PHB/50m%EVA60 (~ -30 ^{o}C, see Figure 4, Table 2). It was argued that the slowing-down of the crystallization kinetics can be associated with a reduction of molecular mobility due to an increase of the glass transition temperature of the system [47]. Another possible reason which still lacks physical confirmation is partial miscibility. As shown in Figure 9 and also elsewhere in [17, 43, 48], where the plots of the normalized crystallinity, X_t, as a function of crystallization time is clearly depicted as being strongly dependent on composition. These plots indicate that for immiscible blends [17,43,48, 49] the profiles for X_t vs. t converge while for miscible blends (examples PHB/PVAC [16], poly(butylenesuccinate-co-butyleneadipate)/poly(vinyl phenol) blends [50]) the profiles diverge.

$t_{1/2}$ for 50m%PHB/50m%EVA91is considerably the longest one, $t_{1/2}$ equals 2720 s (see Figure 7). This is easily attributed to the fact that EVA 91 is miscible with PHB. Moreover, the addition of EVA91 to PHB will result in both dilution of PHB chains at the crystal growth front and reduction of mobility of the PHB chains due to the higher T_g of the blend than that of pure PHB, and then cause a higher activation barrier for PHB crystallization in the blends. Similar results are reported for PHB/PVAC [14-16].
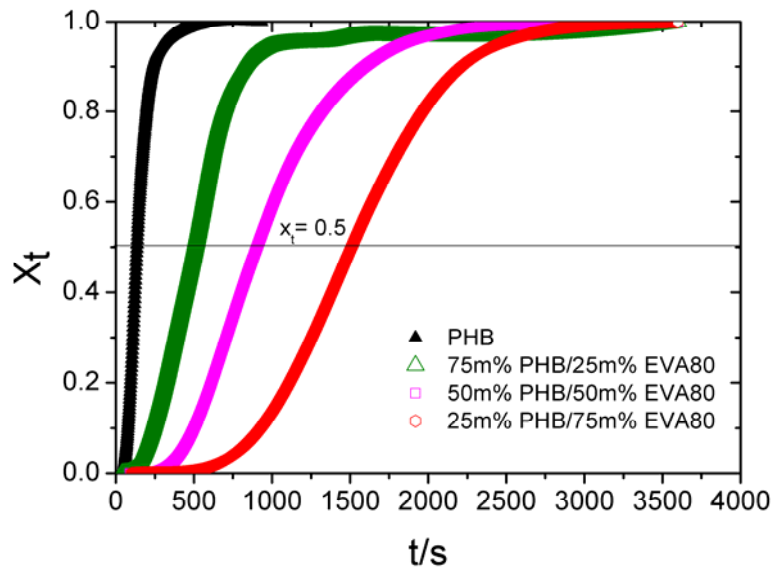
Fig. 9. Normalized relative crystallinity X_t for PHB/EVA80 blends at crystallization temperature 80 $^{\circ}$C with different compositions. The composition is given in the legend.

Conclusions

From the data shown the following conclusions can be drawn:

- The miscibility of PHB with EVA strongly depends on the content of vinyl acetate in the EVA copolymer within the range EVA40 (40m% vinyl acetate) and EVA91 (91m% vinyl acetate). The blends of PHB/EVA91 are completely miscible in the entire (0 to 100m%) compositional ranges. Blends PHB/EVA, for VA varied from 40 till 70m% are immiscible

- The crystallization half time ($t_{1/2}$) of PHB in PHB/EVA blends increases with increasing glass transition temperature (T_g) and decreasing nucleation density.

- it has been shown that the dependence of $t_{1/2}$ on the concentration can be used as an indicator of the extent of miscibility of these particular blends, such that as the X_t vs. t profiles converge immiscibility can be assumed while for diverging profiles miscibility can be assumed.

Experimental part

Materials and blend preparation

Pure bacterial isotactic poly-(R)-hydroxybutyrate (PHB) was kindly supplied by Biomer Company, Krailling, München, Germany [38]. The PHB content is given as >98%, the content of polyhydroxyvalerate (PHV) <1%, and the remaining cell membrane and membrane lipids content about 1%. PHB was obtained as a powder and used as received without further purification.

Ethylene vinyl acetate copolymer (EVA) was supplied by Lanxess Company Leverkusen Germany [39]. EVA was obtained as granules and used as received without further purification. The ethylene vinyl acetate copolymers have a weight

percentage of vinyl acetate ranging from 9m% till 91m%. For simplicity ethylene vinyl acetate copolymer will be nominated as EVA9, where the number indicates m% of vinyl acetate in the EVA copolymer.

Blends of PHB with ethylene vinyl acetate copolymer, where vinyl acetate content varied from 40m% to 91m% were prepared by a film casting method from a chloroform solution. The solvent was allowed to evaporate in air for 14 days and the resulting films were further dried in vacuum at 80 °C for 2 days. In this way, blends were prepared with various PHB/EVA compositions ranging from 75m%PHB/25m%EVA to 25m%PHB/75m%EVA. A blend of PHB with ethylene vinyl acetate copolymer, where vinyl acetate content is e.g. 40m%, will be nominated as PHB/EVA40.

Thermal measurements

In order to obtain information about the thermal behavior (glass transition temperature, melting and crystallization behavior) of ethylene vinyl acetate copolymers EVA in blends with PHB, DSC runs were conducted using a DSC TA Q100 apparatus with Tzero technique from TA Instruments at the German University in Cairo. Temperature and heat flow were calibrated as usual [40] using indium and sapphire as calibrants.

EVA samples were cut in about 6 mg pieces, heated from –50 °C to 130 °C to remove its thermal history and cooled to -50 °C with cooling rate 20 K/min, reheated to 130 °C with heating rate 20 K/min. PHB/EVA blend samples of 3 to12 mg were cut from cast films, heated from –50 °C to 200 °C to remove thermal history and cooled to -50°C with cooling rate 20 K/min, reheated to 200 °C with heating rate 20 K/min. Glass transition temperature, melting temperature and melting enthalpy were evaluated from the second heating run.

Moreover, isothermal crystallization was investigated using a power compensation differential scanning calorimeter, Perkin Elmer Pyris 1 at the University of Rostock. Isothermal measurements were conducted as follows: The sample was first melted at 200 °C for 1 min to erase previous thermal history. Then the sample was cooled with 60 K/min to a temperature between 30 °C to 110 °C, kept at this temperature for 60 min, cooled to 25 °C with cooling rate 60 K/min. In order to get the corresponding melting enthalpy of the crystallized sample, samples were heated with 15 K/min to 200 °C. The melting enthalpy was obtained from peak integration using a straight base line.

Polarized light microscopy

In order to study the effect of EVA on nucleation density and morphology of PHB spherulites in the blend samples, films of 3 µm thickness were mounted on glass slides and covered by cover slips. The morphological study was carried out after melting the sample at 200 °C for 3 min, rapid cooling to 80 °C and keeping it there for 60 min. Optical micrographs were taken by using a Zeiss Microscope Imager MAT polarizing microscope with lens 20X.

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