Crystallization behavior of poly(hydroxybytyrate-*co*-valerate) in model and bulk PHBV/kenaf fiber composites

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Abstract The kinetics of non-isothermal crystallization and melting behavior of poly(hydrohybutyrate-*co*-valerate) (PHBV) in model, bulk and compatibilized (PHBV)/kenaf fiber composites were investigated using differential scanning calorimetry (DSC). Analysis of the non-isothermal crystallization data was carried out based on the Avrami and Mo's models. Activation energies of the crystallization process were determined by the Kissinger approach, and were in the range between 41 and 48 kJ/mol for all investigated samples. It was shown that the kenaf fibers, as well as their content, do not affect significantly the crystallization kinetics of PHBV matrix. The results indicate that crystallization behavior of polymer resin in bulk composites is not affected by the melt processing, thus suggesting absence of degradation processes.

Introduction

Poly(hydrohybutyrate-*co*-hydrohyvalerate) (PHBV) co-polymers have received significant scientific attention due to the fact that they are biodegradable, and their properties can be easily controlled by the content of hydroxy valerate (HV). Depending on the HV content, PHBV copolymers

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can display physical properties and processing behavior resembling polyethylene or polypropylene, and can range from brittle plastics to elastomers. PHBV copolymers with different content of hydroxyvalerate have been used recently as matrices in eco-composites [1, 2], where different natural fibers were applied as reinforcement.

Processing of semi-crystalline polymer composites is usually performed under non-isothermal conditions, and heating/cooling cycles ultimately determine the morphology of the polymer, and consequently, the final properties of the product. Incorporation of fibers, including the natural ones, can significantly influence the crystallization behavior of the matrix, as well as the crystalline morphology [3, 4].

Avella et al. have studied the microstructure and crystallization behavior of PHB, PHBV blends and their composites with different fibers [5]. Thermal characterization of PHBV/wheat fibers composites has evidenced that the presence of straw fibers increases the rate of PHBV crystallization due to a nucleating effect, while the overall crystallinity remains unchanged. Besides the different crystallization behavior, neat PHBV and composite samples exhibit significant differences in melting behavior. The examination of PHBV based model composites with pineapple leaf fibers has shown that the presence of fibers did not affect the crystallization kinetics of the matrix and the degree of crystallinity [6]. The authors have concluded that this is due to poor fiber/matrix interfacial bonding, as indicated by the low interfacial shear strength of 8.23 MPa. On contrary, Reinsch and Kelley have reported that short wood fibers act as nucleating sites for the crystallization of PHBV and enhance its crystallization rate [7]. Dynamic crystallization experiments have shown that the rate of thermally induced crystallization of PHB and its copolymers (containing 8% and 24% valerate) was enhanced as a

result of fiber reinforcement. Bleached kraft, thermomechanical pulp, and microcrystalline cellulose enhance the crystallization rate of PHB and PHBV from both the glassy state and melt. Hot-stage microscopy studies show that polymer crystallites are nucleated on the fiber surface. Sanadi et al. have found that the coupling agent changes the crystallization and melting behavior of kenaf fiber/polypropylene and ethylene–polypropylene composites: the crystallization of the coupled blends was slower than of the uncoupled ones, resulting in lower crystallization temperature and reduced crystallinity [8]. However, for blends with lower molecular weight of PP, the opposite effect was detected by differential scanning calorimetry (DSC). The coupling agent enhances the crystallization of the matrix, and results in higher crystallization temperature and increased crystallinity.

Obviously, contradictory data exists regarding the influence of natural fibers on the crystallization behavior of thermoplastic polymers, as well as on the polymer morphology formed near the fiber surface. However, in cases when nucleating effect of the fibers is found, and transcrystalline layer on the fiber surface is observed, its influence on the mechanical properties of the composites is usually confirmed [9, 10].

In our previous paper we have studied the crystallization behavior of polyhydroxybutyrate (PHB) in model composites with kenaf fibers [11]. The nucleation activity of kenaf fibers was confirmed, affecting the crystallization kinetics of PHB matrix. Recently, we have shown that the use of polymer compatibilizing agent in PHBV/kenaf fibers composites, produced by reaction blending and extrusion, has resulted in enhanced interfacial adhesion, as well as improved mechanical properties [12].

The main goal of this paper is to give a comparative analysis of the crystallization and melting behavior of PHBV resin in PHBV/kenaf fibers model and bulk composites, with and without compatibilizer, and to investigate the applicability of several methods commonly used for analysis of non-isothermal crystallization data obtained by DSC. Moreover, this study would discuss if the results related to model composites can be taken as relevant for further optimization of the processing conditions for bulk composites.

Experimental

Materials

PHBV, a product of Biomer, containing 13% (mol) of hydroxyvalerate, was used as received. Kenaf fibers with average length of 5.1 mm, kindly supplied by Eco Fibers,

Italy, were dried in a vacuum oven at 80 °C for 24 h before use.

Preparation of PHBV composites

Model and bulk composites containing 20 and 30 wt% of kenaf fibers were investigated in this study. The model composites were prepared directly in DSC aluminum pans, while the bulk composites were produced by melt mixing in a Brabender (Rheocord EC of Haake Inc., New Jersey, USA) at 170 °C, increasing progressively the mixing speed up to 32 rpm. Compatibilized PHBV/kenaf fiber composites were prepared by using a mixture of neat and modified PHBV matrix. Modified PHBV, obtained by introducing maleated groups onto its backbone, as reported in our previous paper [12], was used as compatibilizing agent (CA) for PHBV. The compatibilized systems were prepared in a Brabender like apparatus under the same conditions as bulk composites. PHBV and the compatibilizing agent were mixed for 3 min, then dry kenaf fibers were added, and the mixture was blended at 170 °C for further 7 min, increasing progressively the mixing speed up to 32 rpm. All investigated model, bulk and compatibilized (bulk) systems are coded in Table 1.

Calorimetric analysis

The crystallization behavior of the prepared composites was followed using Perkin-Elmer DSC 7 Scanning Calorimeter. The samples were first heated up to 170 °C with a heating rate of 10°/min, and kept at the end temperature for 1 min, in order to erase the thermal history of the samples (I run). The samples were then cooled at constant cooling rates of 40, 20, 15, 10 and 5°/min up to 0 °C (II run). The crystallized samples were reheated up to 170 °C with a heating rate of 10°/min (III run).

Table 1 Codes of the composite samples and relative amount of their components

Codes	Relative amount (% in weight)		
	PHBV	CA	Kenaf
PHBV$_m$	100	0	0
PHBV$_b$	100	0	0
PHBV80$_m$	80	0	20
PHBV70$_m$	70	0	30
PHBV80$_b$	80	0	20
PHBV70$_b$	70	0	30
PHBV75/ca	75	5	20
PHBV65/ca	65	5	30

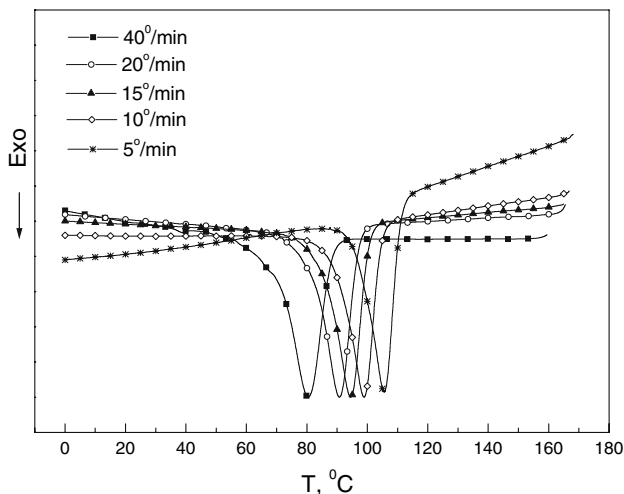m—denotes model composite, b—bulk composites, and CA—compatibilizing agent

Results and discussion

Different approaches were used for the analysis of non-isothermal crystallization of semi-crystalline polymers, among which the Ozawa and modified Avrami methods were the most frequently applied [13]. An et al. have studied the non-isothermal crystallization kinetics of PHB [14], comparing several kinetics methods. They have found that non-isothermal crystallization of PHB from melt and glassy state has shown different rate-dependant characteristics. The Ozawa analysis failed due to the quasi-isothermal nature of the treatment. The new Mo's method, based on the combination of Avrami and Ozawa equations, has been proved as suitable for handling the non-isothermal crystallization of PHB [14].

In this paper detailed comparative analysis of the crystallization and melting behavior of PHBV in model and bulk composites will be given. The aim of such a detailed analysis is to give an answer if significant changes exist in phase behavior of the composites depending on their preparation. Possible negligible differences in the results could lead to replacement the more expensive bulk composites research with a cost-effective lab-scale optimization of the processing conditions.

Non-isothermal crystallization process

The crystallization exotherms for PHBV80$_m$ at five different cooling rates are presented in Fig. 1. It is obvious that by increasing the cooling rates, exothermic peaks become wider and shifted to lower temperatures, as expected. This observation is generally true for all investigated systems (model, bulk, and compatibilized composites). The characteristic data, crystallization temperatures, T_p (temperature at the maximum crystallization peak) and the degrees of crystallinity, x_c, are collected in Table 2. The degree of crystallinity is calculated according to the relation $x_c = \Delta H_f / \Delta H_f°$, where ΔH_f is the enthalpy of fusion, and $\Delta H_f°$ is taken as 109 J/g [15]. It could be noted that the crystallization temperatures of model composites are slightly decreased when compared to T_p of pure matrix, while the degrees of crystallinity when compared to x_c of PHBV at cooling rates between 15 and 5°/min are insignificantly higher. At the same time, it can be assumed that at cooling rates lower than 40°/min, the content of kenaf fibers of 20–30 wt% has almost negligible influence on T_p and x_c. For example, identical degrees of crystallinity of 45% and crystallization temperatures of 106 °C are determined for both PHBV80$_m$ and PHBV70$_m$ composites, at a cooling rate of 5°/min.

The results, obtained from non-isothermal crystallization of bulk composites, are collected in Table 3, and similar conclusions can be derived as for the model composites. Insignificant changes of T_p and x_c are detectable in all bulk composites. A slight decrease of T_p in model composites, and almost negligible changes of T_p in bulk composites, when compared to pure matrices, could be an indication that the presence of kenaf fibers does not have any significant influence on the crystallization behavior of PHBV matrix. This is opposite to our earlier findings for the nucleation activity of kenaf fibers in PHB/kenaf model

Fig. 1 Crystallization exotherms of PHBV80$_m$ model composite at different cooling rates

Table 2 Crystallization parameters obtained from non-isothermal crystallization DSC curves for PHBV/kenaf fiber model composites
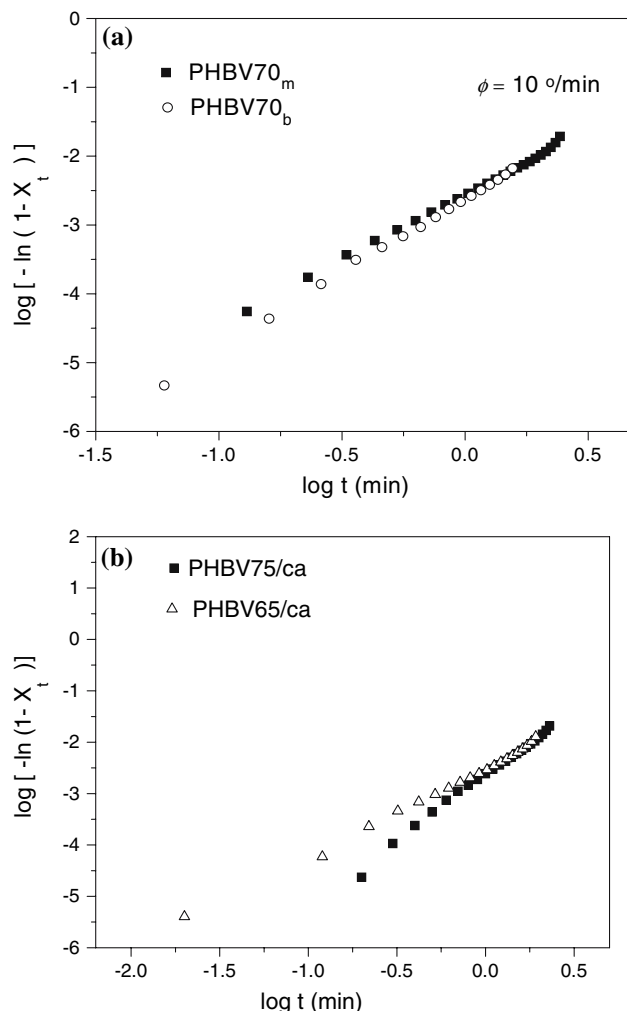
ϕ (°/min)	PHBV$_m$			PHBV80$_m$			PHBV70$_m$		
	T_p (°C)	ΔH_c (J/g)	x_c (%)	T_p (°C)	ΔH_c (J/g)	x_c (%)	T_p (°C)	ΔH_c (J/g)	x_c (%)
40	83	−42	39	81	−43	39	81	−39	36
20	93	−46	42	91	−45	41	91	−42	39
15	97	−44	40	95	−47	43	95	−45	41
10	102	−45	41	99	−46	42	99	−47	43
5	109	−46	42	106	−49	45	106	−49	45

Table 3 Crystallization parameters obtained from non-isothermal crystallization DSC curves for PHBV/kenaf fiber bulk composites

ϕ (°/min)	PHBV$_b$			PHBV80$_b$			PHBV70$_b$		
	T_p (°C)	ΔH_c (J/g)	x_c (%)	T_p (°C)	ΔH_c (J/g)	x_c (%)	T_p (°C)	ΔH_c (J/g)	x_c (%)
40	85	−41	38	84	−40	37	85	−44	40
20	95	−45	41	94	−45	41	94	−48	44
15	98	−48	44	98	−47	43	97	−49	45
10	101	−47	43	102	−47	43	101	−48	44
5	109	−47	43	109	−51	47	112	−51	47

composites, where the presence of fibers influenced the crystallization behavior of the matrix [11].

It must be pointed out that the crystallization temperatures and degrees of crystallinity (T_p and x_c) of bulk composites are slightly higher compared to those of model composites. This is probably due to the better interfacial adhesion, i.e., better contact between the matrix and the fibers existing in bulk composites, as a result of the processing conditions (mixing, extrusion, pressing).

Very similar results to those presented for bulk composites are obtained for compatibilized systems (Table 4). It can be assumed that the compatibilizing agent has a minor effect on the crystallization behavior of PHBV, although its influence on the adhesion strength and overall mechanical properties of PHBV/kenaf fiber composites, reported in our preceding paper [12], is indisputable.

Non-isothermal crystallization kinetic analysis based on different methods

In our previous paper we have shown that the modified Avrami model, Mo's analysis, as well as Kissinger approach, can satisfactorily describe the non-isothermal crystallization kinetics of PHB [11], which was an additional reason to investigate the applicability of these models for PHBV systems.

Avrami equation [16–18] was used to analyze the non-isothermal crystallization kinetic:

$$1 - X(t) = \exp(-kt^n) \tag{1}$$

where $X(t)$ is the relative crystallinity at time t, k is the crystallinity rate constant, and n is the Avrami exponent, depending on the nucleation mechanism and the dimension of crystal growth. For non-isothermal crystallization, the relative crystallinity $X(T)$ is a function of temperature, and the time is related to temperature formulated as [19]:

$$t = \frac{|T_0 - T|}{\phi} \tag{2}$$

Table 4 Crystallization parameters obtained from non-isothermal crystallization DSC curves for PHBV/kenaf fiber compatibilized composites

ϕ (°/min)	PHBV75/ca			PHBV65/ca		
	T_p (°C)	ΔH_c (J/g)	x_c (%)	T_p (°C)	ΔH_c (J/g)	x_c (%)
40	84	−45	41	86	−45	41
20	94	−48	44	95	−50	46
15	98	−49	45	99	−49	45
10	102	−50	46	102	−49	45
5	108	−50	46	108	−52	48

where T_0 is the onset temperature at which the crystallization begins ($t = 0$). According to Eq. 2, the horizontal axis observed in a DSC curve for non-isothermal crystallization data can be converted into time scale.

Using double logarithmic plot of the Avrami equation $\log[-\ln(1 - X_t)]$ against $\log t$ (Fig. 2a, b), two adjustable parameters ($\log k$ and n) can be derived from the intercepts and slopes, respectively. The derived parameters are shown in Tables 5, 6, and 7. Considering the non-isothermal character of the crystallization process, parameter k can be adequately corrected to obtain the corresponding rate constant k_c at cooling rate ϕ, thus receiving Jeziorny rate constant [20] defined as

$$\log k_c = \frac{\log k}{\phi} \tag{3}$$

The values of k_c, listed in Tables 5–7, mainly increase with the increase of cooling rates, thus suggesting faster

Fig. 2 (a) Avrami plots for PHBV70$_m$ and PHBV70$_b$ composites. (b) Avrami plots for compatibilized systems PHBV75/ca and PHBV65/ca

Table 5 Parameters obtained from Avrami analysis and Jeziorny rate constants for PHBV model composites

ϕ (°/min)	PHBV$_m$				PHBV80$_m$				PHBV70$_m$			
	$\log k$	n	k_c	$t_{1/2}$ (min)	$\log k$	n	k_c	$t_{1/2}$ (min)	$\log k$	n	k_c	$t_{1/2}$ (min)
40	−1.45	1.90	0.92	0.86	−1.41	1.91	0.92	0.70	−1.49	1.90	0.92	0.76
20	−1.90	1.95	0.80	1.69	−2.14	2.45	0.78	1.90	−2.06	1.72	0.79	1.71
15	−2.15	1.88	0.72	2.06	−2.43	2.04	0.68	3.08	−2.22	2.30	0.71	1.95
10	−2.56	1.87	0.55	2.48	−3.15	1.49	0.48	2.74	−2.55	1.90	0.55	3.36
5	−2.92	2.01	0.26	5.14	−3.20	1.48	0.23	3.50	−2.85	1.84	0.27	6.60

Table 6 Parameters obtained from Avrami analysis and Jeziorny rate constants for PHBV bulk composites

ϕ (°/min)	PHBV$_m$				PHBV80$_m$				PHBV70$_m$			
	$\log k$	n	k_c	$t_{1/2}$ (min)	$\log k$	n	k_c	$t_{1/2}$ (min)	$\log k$	n	k_c	$t_{1/2}$ (min)
40	−1.55	2.01	0.91	0.79	−1.57	1.80	0.91	0.80	−1.71	1.70	0.91	0.84
20	−2.33	1.57	0.76	1.50	−2.33	2.30	0.76	1.68	−2.15	1.5	0.78	1.11
15	−2.91	1.99	0.64	1.85	−2.48	1.83	0.68	2.14	−2.34	2.06	0.69	2.02
10	−2.81	1.98	0.50	2.30	−2.61	2.04	0.55	4.31	−2.61	2.17	0.55	2.71
5	−2.88	5.21	0.26	4.74	−2.93	1.80	0.26	4.66	−3.17	1.79	0.23	5.14

Table 7 Parameters obtained from Avrami analysis and Jeziorny rate constants for PHBV compatibilized composites

ϕ (°/min)	PHBV75/ca				PHBV65/ca			
	$\log k$	n	k_c	$t_{1/2}$ (min)	$\log k$	n	k_c	$t_{1/2}$ (min)
40	−1.44	2.03	0.92	0.81	−1.39	1.91	0.92	0.72
20	−2.11	2.34	0.78	1.63	−1.86	2.39	0.81	1.37
15	−2.34	1.57	0.69	2.01	−2.49	2.58	0.68	1.91
10	−2.63	2.40	0.54	3.24	−2.52	1.74	0.56	2.99
5	−2.23	5.21	0.36	5.78	−1.75	2.21	0.45	4.98

crystallization process. This is reasonable, since k, k_c and $t_{1/2}$ (half time of crystallization) are a measure of crystallization rate, which gets faster with supercooling [21]. Furthermore, in model composites it is obvious that for a given cooling rate the rate constant k_c is independent of kenaf fiber content (Table 5). The same conclusion is valid for bulk composites (Table 6). It is interesting to point out that at certain cooling rate, almost identical rate constants are obtained for model and bulk composites. Approximately identical crystallization behavior of polymer resin in model and bulk composites could be evidence that melt processing of bulk composites does not cause any significant thermal degradation of the matrix.

The Avrami parameters n and k were found to have very similar values with those reported earlier for PHB/kenaf fiber composites [11]. The n parameter ranged between 1.48 and 2.45 in model composites, and from 1.5 to 2.3 in bulk composites. Similar values ($n \approx 2$) are obtained for compatibilized PHBV75/ca and PHBV65/ca systems,

indicating again that the presence of a compatibilizer does not affect drastically the kinetic parameters of crystallization.

Mo proposed a model that is actually a modified method, based on both Avrami and Ozawa models [22]. The well-known equation, based on these two models, is given as

$$\log \phi = \log F(T) - a \log t \qquad (4)$$

where $F(T)$ refers to the value of the cooling rate, which is chosen at the unit crystallization time, when the measured system reaches certain relative crystallinity, and a is the ratio of Avrami and Ozawa exponents ($a = n/m$). The kinetic parameters $F(T)$ and a can be estimated by the intercept and slope of the plots $\log \phi$ versus $\log t$ at different cooling rates. According to Eq. 4, at a given degree of crystallinity, the plot of $\log \phi$ against $\log t$ gives a straight line with an intercept of $\log F(T)$ and a slope of $-a$.
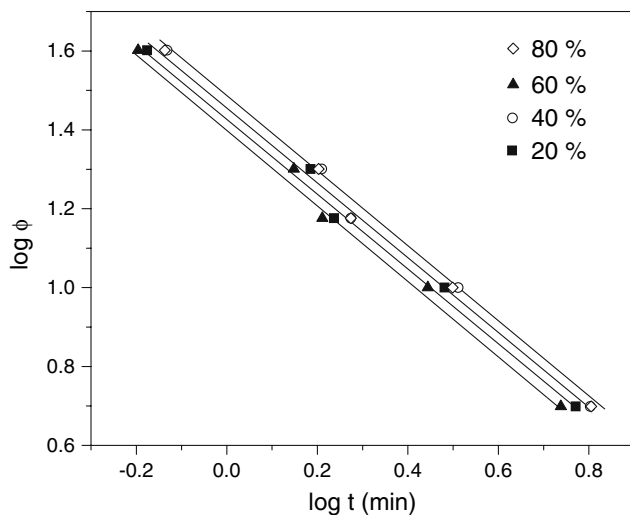
Fig. 3 Plots of log ϕ versus log t for PHBV70$_m$ composite

As it is shown in Fig. 3, plotting of log ϕ against log t gives linear correlation at a given degree of crystallinity. The $F(T)$ and a values are listed in Tables 8, 9, and 10. The $F(T)$ values increase with the relative degree of crystallinity, while the parameter a ranges from 0.95 to 1.19 in model composites, and from 1.0 to 1.17 for bulk composites. Compared to $F(T)$ values for the PHBV matrix, for X_t up to 60% lower values of $F(T)$ are detected for model composites while in bulk composites $F(T)$ values are lower at all X_t only for PHBV70$_b$ composite when compared to PHBV$_b$. The $F(T)$ function has notably lower values for compatibilized systems, especially in PHBV65/ca composite (Table 10). These results suggest that for X_t up to

Table 8 Values of a and $F(T)$ parameters versus degree of crystallinity based on Mo's treatment for PHBV model composites

X_t (%)	PHBV$_m$		PHB80$_m$		PHBV70$_m$	
	$F(T)$	a	$F(T)$	a	$F(T)$	a
20	29.5	1.19	26.0	1.00	27.5	0.95
40	32.4	1.19	28.8	1.04	29.5	0.96
60	34.6	1.19	33.0	1.06	32.4	0.96
80	38.9	1.19	38.9	1.11	36.3	0.96

Table 9 Values of a and $F(T)$ parameters versus degree of crystallinity based on Mo's treatment for PHBV bulk composites

X_t (%)	PHBV$_b$		PHB80$_b$		PHBV70$_b$	
	$F(T)$	a	$F(T)$	a	$F(T)$	a
20	27.3	1.17	28.8	1.00	24.6	1.03
40	29.8	1.17	31.6	1.02	26.9	1.05
60	32.3	1.17	33.8	1.03	29.5	1.06
80	35.4	1.14	37.2	1.01	33.7	1.05

Table 10 Values of a and $F(T)$ parameters versus degree of crystallinity based on Mo's treatment for PHBV model composites

X_t (%)	PHBV75/ca		PHBV65/ca	
	$F(T)$	a	$F(T)$	a
20	29.9	1.04	24.5	1.04
40	31.3	1.04	27.5	1.04
60	33.8	1.06	29.5	1.04
80	37.6	1.03	34.4	1.04

60% the crystallization rate in model composites is increased in the presence of kenaf fibers, while for bulk systems this conclusion is valid only for the PHBV70$_b$ composite. In compatibilized systems, according to $F(T)$ values, the crystallization rate of PHBV resin is enhanced only in PHBV65/ca composite when compared to pure PHBV$_b$, but is unchanged when compared to PHBV70$_b$. These findings are certainly not in a close correlation with the results, obtained by Avrami analysis for model and compatibilized systems, since the Avrami model collects data related to both low and high relative crystallinities. In Mo's analysis, crystallization functions are related to certain X_t values, and from this point of view these results could be taken as more convenient in the non-isothermal crystallization treatment, but again must be considered with care.

## Activation energy of crystallization during non-isothermal process

The activation energy of crystallization is derived by the Kissinger equation [23]. The influence of various cooling rates on the non-isothermal crystallization process is given with the following equation:

$$\frac{d[\ln(\phi/T_p^2)]}{d(1/T_p)} = \frac{\Delta E}{R} \tag{5}$$

where R is the universal gas constant, and T_p is the peak crystallization temperature. The activation energy could be determined by the slope of the $log(\phi/T_p^2)$ versus $1/T_p$ plots, as presented in Fig. 4a and b.

The activation energies range from 40.8 to 43.5 kJ/mol in model composites, and from 41.1 to 45.2 kJ/mol in bulk composites, suggesting that the crystallization behavior is almost independent of the way of composite's preparation. Slightly higher activation energies are determined for compatibilized composites (44.3 and 47.5 kJ/mol for the PHBV75/ca and PHBV65/ca, respectively).

Slight discrepancies of the results might be due to the selection of baseline when converting the crystallization exothermic data into the relative crystallinity as a function of temperature (or time). Generally, the results obtained for
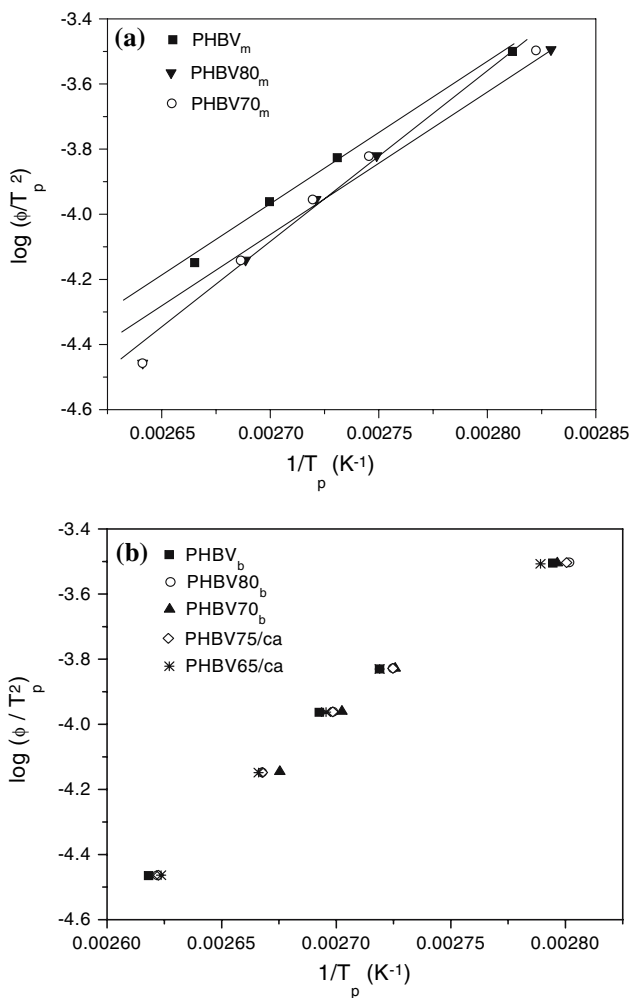
Fig. 4 (**a**) Kissinger plots for evaluation of the non-isothermal crystallization energies for PHBV$_m$ and its model composites. (**b**) Kissinger plots $\log(\phi/T_p^2)$ versus $1/T_p$ for bulk and compatibilized systems

Fig. 5 Subsequent melting endotherms (10 °C/min) for PHBV80$_m$ samples recorded after non-isothermal crystallization at different cooling rates

model, bulk and compatibilized systems are very similar, suggesting minor effects of the kenaf fibers on the crystallization behavior of the PHBV matrix, independent of the way composites were prepared. Very similar to our results, Lio and Netravali have found that pineapple fibers did not affect the crystallization kinetics of PHBV matrix [6]. The authors have concluded that this is due to a poor interfacial bonding between hydrophilic fiber and hydrophobic PHBV, and to the restricted absorption of PHBV molecules on the fiber's surface.

Melting behavior

Figure 5 shows subsequent melting endotherms (10 °C/min) for PHBV80$_m$ samples, recorded after non-isothermal crystallization at different cooling rates.

Double melting peaks at around 145 and 155 °C are apparently observed after non-isothermal crystallization at
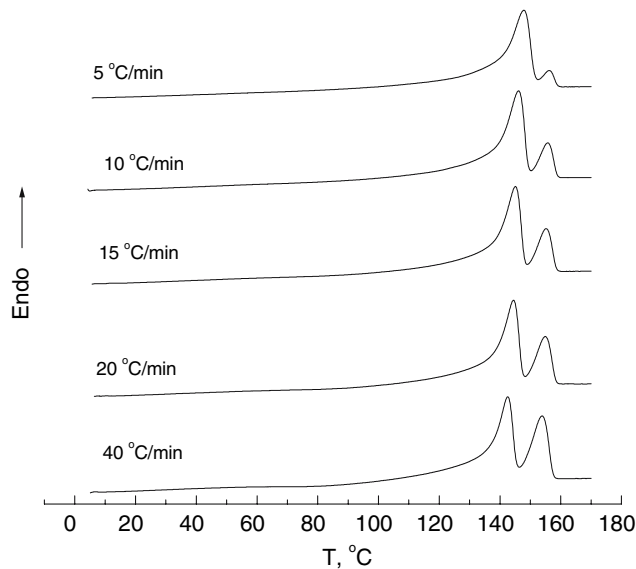
all investigated cooling rates, which is consistent with the earlier published results [24, 25]. The same trend is observed in all model, bulk, and compatibilized composites. The occurrence of a lower melting peak was postulated to be a result of melting of the primary crystallites, while the upper melting peak was attributed to the melting of recrystallized crystallites of different stability [26].

The melting temperatures (measured in III run as T_{m1} and T_{m2}) and corresponding degrees of crystallinity are reported in Table 11a, b, and c. It is evident that the position of T_{m1} peaks decreases with the increase of cooling rates, while the position of T_{m2} peaks did not seem to be affected to a great extent by the changes in cooling rates. It is also apparent that changes in the cooling rate affected the position of T_{m1} more than that of T_{m2}. Generally, the degrees of crystallinity are higher at lower cooling rates, while the enthalpies of fusion, relevant to T_{m2} melting peaks, decrease. This could be an indication that at lower crystallization rates, crystallization in these systems proceeds with a higher degree of completion. Therefore the amount of recrystallized crystallites is significantly lower (lower ΔH_2 values) when compared to recrystallized species, relevant to higher cooling rates (higher values of ΔH_2).

It is obvious from Table 11a that melting temperatures in model composites are not influenced by the kenaf fiber content, while a slight decrease of their values is notable when compared to pure PHBV$_m$ matrix. At the same time, degrees of crystallinity of PHBV80$_m$ and PHBV70$_m$ are lower, compared to PHBV$_m$ matrix crystallized at each cooling rate. The same melting behavior can be detected

Table 11 Melting parameters obtained from the III run for (a) model composites, (b) bulk composites, and (c) compatibilized systems

ϕ (°C min^{-1})	PHBV$_m$					PHBV80$_m$					PHBV70$_m$				
	T_{m1} (°C)	ΔH_1 (J/g)	x_c (%)	T_{m2} (°C)	ΔH_2 (J/g)	T_{m1} (°C)	ΔH_1 (J/g)	x_c (%)	T_{m2} (°C)	ΔH_2 (J/g)	T_{m1} (°C)	ΔH_1 (J/g)	x_c (%)	T_{m2} (°C)	ΔH_2 (J/g)
(a) Model composites															
40	143	33	30	155	16	142	25	23	154	14	142	27	25	154	15
20	145	41	38	156	12	144	34	31	155	11	144	35	32	155	11
15	146	44	40	156	10	144	35	32	155	10	145	38	35	155	9
10	148	43	39	157	6	146	39	36	156	7	146	39	36	156	7
5	150	44	40	157	1	147	41		156	2	148	43	39	156	2
(b) Bulk composites	PHBV$_m$					PHBV80$_m$					PHBV70$_m$				
40	143	40	37	154	17	143	38	35	155	16	137	18	17	149	19
20	145	44	40	155	12	145	43	39	156	11	138	20	18	150	15
15	146	45	41	156	9	146	44	40	156	8	139	19	17	150	13
10	147	46	42	156	5	147	43	39	156	5	140	23	21	150	10
5	149	47	43	159	2	149	46	42	157	2	142	28	26	151	4
(c) Compatibilized systems	PHBV75/ca					PHBV65/ca									
40	143	39	36	155	17	142	40	37	155	20					
20	145	44	40	156	12	144	44	40	156	14					
15	146	45	41	156	9	145	44	40	156	10					
10	147	44	41	156	5	146	42	39	156	6					
5	149	46	42	156	2	148	46	42	156	1					

for bulk composites. Decreasing values of the first melting temperatures (T_{m1}), as well as lower degrees of crystallinity could be identified in PHBV70$_b$ composite, when compared to PHBV$_b$ matrix. In compatibilized samples, the melting temperatures and the degrees of crystallinity are not influenced by the presence of compatibilizing agent, which is consistent with the crystallization data for these systems.

Following the presented results, it is obvious that the presence of kenaf fibers in model and bulk composites, as well as in compatibilized samples, does not have significant influence on the melting behavior of the samples, with several exceptions related to PHBV70b composite.

Conclusions

The non-isothermal crystallization behavior of PHBV matrix in model, bulk, and compatibilized composites was investigated by DSC. Analysis of the obtained data was carried out based on Avrami, Jeziorny, and Mo's analysis, as well as Kissinger approach. The results obtained from the Avrami analysis suggest that kenaf fibers and the introduction of maleated groups onto PHBV bones do not affect significantly the crystallization kinetics of PHBV matrix in model, bulk, and compatibilized systems. It was

shown that the processing conditions, i.e. different cooling rates (20–5 °C/min), practically do not have significant influence on the crystallization process.

The almost identical crystallization behavior of polymer resin in model and bulk composites suggests that certain melt processing of bulk composites does not lead to degradation processes.

References

1. Shibata M, Takachiyo KI, Ozawa K, Yosomiya R, Takeishi H (2002) J Appl Polym Sci 85:129
2. Mohanty AK, Khan MA, Sahoo S, Hinrichsen G (2000) J Mater Sci 35:2589
3. Joseph PV, Joseph K, Thomas S, Pillai CKS, Prasad VS, Groeninckx G, Sakissova M (2003) Compos Part A 34:253
4. Avella M, Martuscelli E, Raimo M (2000) J Mater Sci 35:523
5. Avella M, La Rota G, Martuscelli E, Raimo M, Sadocco P, Elegir E, Riva R (2000) J Mater Sci 35:829
6. Luo S, Netravali AN (1999) Polym Compos 20:367
7. Reinsch V, Kelley S (1997) J Appl Polym Sci 64:1785
8. Feng D, Caulfield DF, Sanadi AR (2001) Polym Compos 22:506
9. Reinsch VE, Rebenfeld L (1994) J Appl Sci 52:649
10. Desio GP, Rebenfeld L (1992) J Appl Sci 44:1989
11. Buzarovska A, Bogoeva-Gaceva G, Grozdanov A, Avella M (2006) J Appl Polym Sci 102:804
12. Avella M, Bogoeva-Gaceva G, Buzarovska A, Errico M, Gentile G, Grozdanov A (in press) J Appl Polym Sci
13. Di Lorenzo ML, Silvestre C (1999) Prog Polym Sci 24:917

14. An Y, Dong L, Mo Z, Liu T, Feng Z (1998) J Polym Sci Part B Polym Phys 36:1305
15. Scandola M, Focarete ML, Adamus G, Sikorska W, Baranowska I, Swierczek S, Gnatowski M, Kowalczuk M, Jedlinski Z (1997) Macromolecules 30:2568
16. Avrami MJ (1939) J Chem Phys 7:1103
17. Avrami MJ (1940) J Chem Phys 8:212
18. Avrami MJ (1941) J Chem Phys 9:177
19. Patel RM, Bheda JH, Spruiell J (1991) J Appl Sci 42:1671
20. Jeziorny A (1978) Polymer 19:1142
21. Mandelkern L (2004) Crystallization of polymers, 2nd edn, vol 2. Cambridge University Press, Cambridge
22. Liu T, Mo Z, Wang S, Zhang H (1997) Polym Eng Sci 37:568
23. Kissinger HE (1957) Anal Chem 11:1702
24. Bassett DC, Olley RH, Al Raheil IAM (1988) Polymer 29:1745
25. Organ SJ, Barham PJ (1991) J Mater Sci 26:1368
26. Bell JP, Murayama TJ (1969) J Polym Sci 7(A-2):1059