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Crystallization kinetics of poly(hydroxybutyrate-*co*-hydroxyvalerate) and poly(dicyclohexylitaconate) PHBV/PDCHI blends: thermal properties and hydrolytic degradation

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Abstract The influence of poly(dicyclohexylitaconate) (PDCHI) content, on the crystallization kinetics, thermal properties, and hydrolytic degradation of poly(hydroxybutyrate-*co*-hydroxyvalerate), PHBV, was studied. Irrespective of the blend composition, the calorimetric and FTIR spectroscopy analyses indicate that the blend components are immiscible. The kinetics of non-isothermal crystallization and melting behavior of PHBV were studied by differential scanning calorimetry (DSC) and examined using non-isothermal Avrami and Mo's analyses. Based on Mo's model, the PDCHI content has significant effect on the crystallization kinetics of PHBV matrix. Despite the immiscibility of these polymers, the amorphous polyvinyl ester could extensively control the rate of hydrolytic degradation.

Introduction

In the last ten years, the scientific research on biodegradable plastics from renewable resources has been intensified [1, 2]. This was mainly due to the fact that large-scale production of oil-derived plastics generates enormous quantities of plastic waste. This represents an acute problem, since most of the traditional plastics are not biodegradable or recyclable, while for the majority of recyclable plastics the recycling process is economically, ecologically, or energetically unjustified. An additional and very important reason for increased interest in biodegradable polymers is the fact that petroleum resources are finite.

From this point of view, considerable scientific attention has been focused on biodegradable polymers, poly(vinyl alcohol), poly(caprolactone), poly(lactic acid), as well as polymers and copolymers based on poly(hydroxyalkanoates) [3, 4]. For example, polyhydroxyalkanoates (PHA), as representatives of biosynthetic polymers, are aliphatic polyesters naturally produced via microbial process on sugar-based medium, where they act as carbon and energy storage material in bacteria [5]. More than hundred different monomers can be combined within this family to obtain materials with extremely diverse properties. Polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), and their copolymers poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) are commonly used polymer matrices in numerous eco-composites [6, 7]. They were the first biodegradable polyesters to be utilized in plastics, since they are biodegradable, and at the same time have very similar mechanical and thermal properties to polyolefins (PP and PE) [8]. Despite these positive properties, their high price is still a high barrier for their wider application.

Many composites based on PHB and PHBV have been developed in order to improve some of their properties (thermal stability, gas barrier properties, strength, low melt viscosity, and slow biodegradation rate), as well as to reduce their high price by introducing low-cost natural fibers and different fillers from agricultural renewable resources [9–12]. Special emphasis has been paid to compatibilization strategies, as well as novel approaches of introducing organic and inorganic nano-fillers in order to obtain increased barrier properties [13].

Blending of biodegradable polymers (BP) has been proved as a common approach in tailoring their properties [14, 15]. Regardless of whether a miscible or immiscible

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blend is to be obtained, the second polymer could significantly control the biodegradability of BP. Since PHBV degradation depends on the degree of crystallinity, the second polymer in the appropriate blend could have certain influence on the rate of degradation. PHBV has been blended with various biodegradable and non-biodegradable polymers in order to improve its physical and mechanical properties.

Amorphous polyesters based on itaconic acid could be interesting materials as a second component in PHBV mixtures, since these polymers indicate potential process of biodegradation in the appropriate blends. Moreover, poly(dicyclohexylitaconate) (PDCHI), as amorphous polymer belonging to this class of polymers, has relatively high T_g (around 140 °C) depending on its molecular weight [16]. From this point of view, the crystallization process of PHBV will be performed at crystallization temperature below the T_g of PDCHI, i.e., in the presence of glassy polymer. The addition of PDCHI to PHBV, due to the higher value of glass transition temperature of this polymer, could give interesting modifications to the PHBV properties.

The aim of this article is to prepare PHBV/PDCHI blends, and to investigate the influence of the amorphous polymer with relatively high glass transition on the crystallinity and crystallization kinetics of PHBV. Furthermore, the degradation of the polymer blends in strong base medium will be analyzed.

Experimental

Materials

PHBV a product of Biomer (Krailling-Germany) containing 13% hydroxyvalerate with molecular weight of $M_w = 420$ kDa was used as received. The synthetic itaconate polyvinylester, PDCHI with low molecular weight was laboratory synthesized according to the procedure reported elsewhere [16]. The molecular weights of synthesized polyitaconate, determined by GPC analysis, are $M_n = 28000$ g/mol and $M_w = 58000$ g/mol.

Blend preparation

PHBV/PDCHI polymer blends with different weight ratios (80/20, 70/30, 50/50 w/w) were prepared by casting from chloroform. The solutions were prepared by dissolving 15% (w/v) of each polymer in hot chloroform and stirring for 5 h. The mixtures were then poured into Petri dishes, and the solvent was allowed to evaporate. The films were dried in vacuum oven for 24 h. All the investigated samples are coded in Table 1.

Table 1 Codes of investigated samples and relative amount of their components

Code	Relative amount (wt%)	
	PHBV	PDCHI
PHBV	100	0
PHBV80	80	20
PHBV70	70	30
PHBV50	50	50
PDCHI	0	100

Characterization

Differential scanning calorimetry (DSC)

Thermal properties and the kinetics of crystallization of the homopolymers and blend films were analyzed by differential scanning calorimetry (PERKIN ELMER DSC 7).

The blend films were first heated from −20 to 170 °C, kept for 1 min in order to erase the thermal history of the samples, and cooled at different cooling rates of 40, 20, 10, and 5°/min. The crystallized samples were reheated up to 170 °C with a heating rate of 10°/min. The degree of crystallinity of each sample was calculated according the relation $x_c = \Delta H_f / \Delta H_f^\circ$, where ΔH_f is the enthalpy of fusion and ΔH_f° is taken as 109 J/g [17].

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of PHBV/PDCHI films were measured by ATR reflection method, in which 64 scans were averaged at a resolution of 4 cm^{-1}, using Perkin-Elmer (Spectrum 100) FTIR instrument.

Hydrolytic degradation

Thin films with dimensions 10 × 10 × 0.5 mm were cut and kept in 0.1 M NaOH at various time intervals. After each period of degradation, the samples were removed, washed with distilled water, and vacuum dried for 48 h. The weight loss was calculated by the following equation,

$$W_{\text{loss}}(\%) = \frac{W_0 - W_t}{W_0} \times 100$$

where W_0 is the initial weight of the polymer film, and W_t is the weight loss at the time t of exposure in NaOH solution.

Results and discussion

Thermal and crystallization behavior

The thermal properties, as well as crystallization kinetics, were investigated in dynamic conditions in order to obtain useful information for potential industrial application of these systems. In general, the miscibility of two polymers is related to detection of a single T_g between the T_gs of pure components, investigated by DSC.

From the first heating scans for all investigated samples, the T_gs of the two components or even a single T_g were undetectable. This could be explained by the very fast crystallization and also by the fact that the T_g of PDCHI is close to the melting temperature onset of PHBV.

Figure 1 shows the DSC thermograms of the PHBV blend films at a cooling rate of 10°/min. Single crystallization peaks can be observed for all blend ratios. It could be noted that the crystallization temperatures (T_c) of PHBV in polymer blend films when compared with the T_c of unblended PHBV have significant decreasing tendency (9–16 °C) with the increase of PDCHI content. This behavior might suggest that the crystallization process of PHBV proceeded with considerable difficulty in the presence of bulky polyvinyl ester [18]. The estimated crystallinity index for PHBV50 (given in Table 2) is lower than that determined for PHBV, while for the other two blends (PHBV80 and PHBV70) x_cs are slightly lower. The DSC curves, obtained from the second heating scans for PHBV blends and unblended PHBV, are presented in Fig. 2. From the DSC melting data collected in Table 2, it could be concluded that the T_ms do not vary significantly with the PDCHI content in the blend, while the melting enthalpies are variable. The melting enthalpies, corresponding to the lower melting peak, have a decreasing tendency with PDCHI content, while those, corresponding to the upper melting peak, have increased values. The first melting peak is due to the melting of crystals formed during the sample preparation, while the second peak is due to the fusion of crystals formed during the heating in the DSC pans [19].

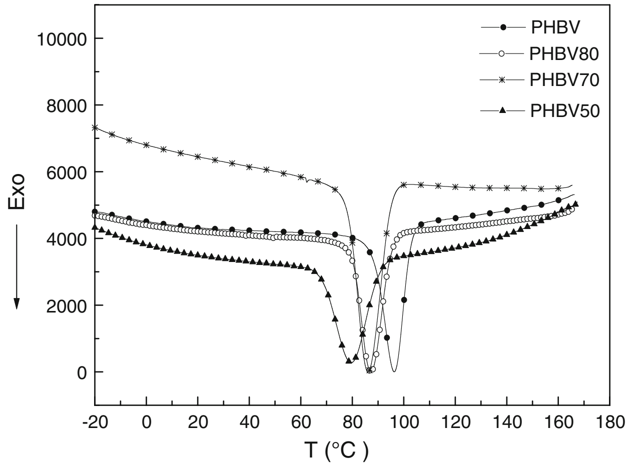

Fig. 1 DSC cooling exotherms (cooling rate of 10°/min) for PHBV and its blends with PDCHI

Table 2 Cooling and melting parameters for PHBV and its blends

Sample	T_c (°C)	x_c	T_{m1}	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)
PHBV	96	44	145	30	155	9
PHBV80	87	40	143	20	154	12
PHBV70	86	42	143	23	155	13
PHBV50	80	36	142	12	154	15

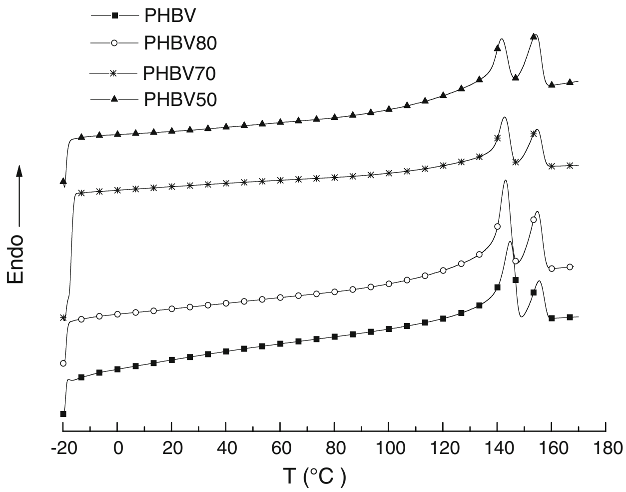

Fig. 2 Melting endotherms (second runs, scanning rate of 10°/min) for PHBV and its blends

From these thermal properties, it could be outlined that the bulky PDCHI has influence on the crystallization process of PHBV, as well as on the amount of crystallized material. The increased ΔH_{m2} enthalpies with the increase of PDCHI content could support the hypothesis that the amount of crystals, formed during the heating process, is increased with the increase of PDCHI content, probably due to the fact that the second polymer undergoes its glass transition, and therefore the increased mobility could result in newly formed crystals during the heating process.

Nonisothermal crystallization kinetics analysis

Figure 3 shows the relative crystallinity, X_t, versus the temperature of PHBV and its blend PHBV70. The relation between the crystallization time, t, and temperature, T, is expressed as $t = \frac{|T_o - T|}{\phi}$, where T_o is the onset temperature at which the crystallization begins ($t = 0$), and ϕ is the cooling rate [20]. According to the last equation, the horizontal axis, observed in a DSC curve for the nonisothermal crystallization data, can be converted into a time scale (Fig. 4). The characteristic Avrami plots log [−ln (1 − X_t)] versus log t [21–23] for the PHBV70 blend at various cooling rates are presented in Fig. 5. Similar graphs are obtained for all investigated samples. The two adjustable Avrami parameters, derived from the slopes and intercepts of each line, were calculated and collected in Table 3. The corrected k_c

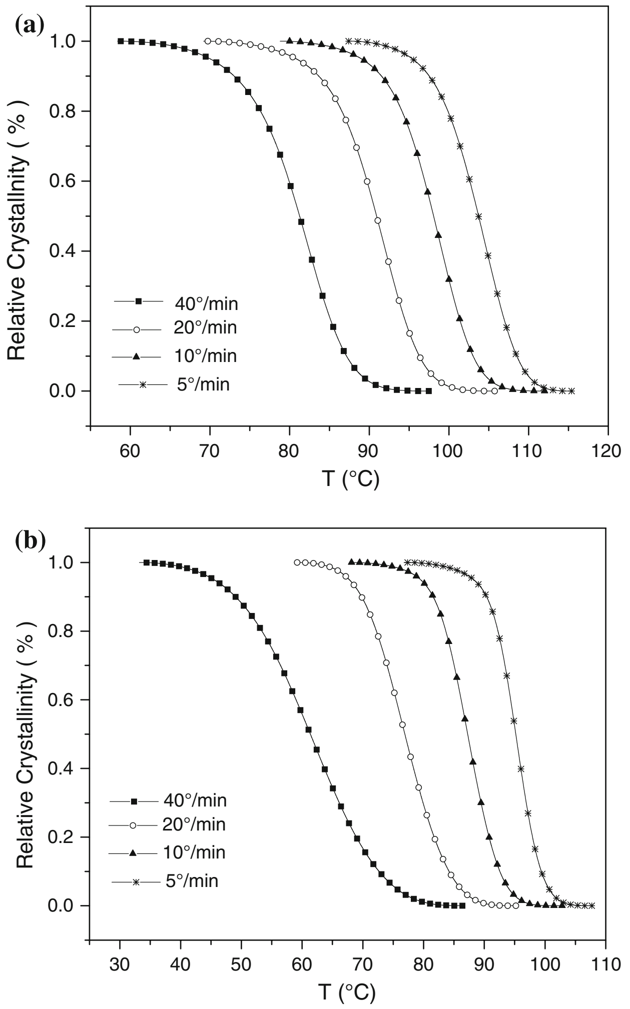

Fig. 3 Relative crystallinity as a function of temperature **a** PHBV film, **b** PHBV70 film

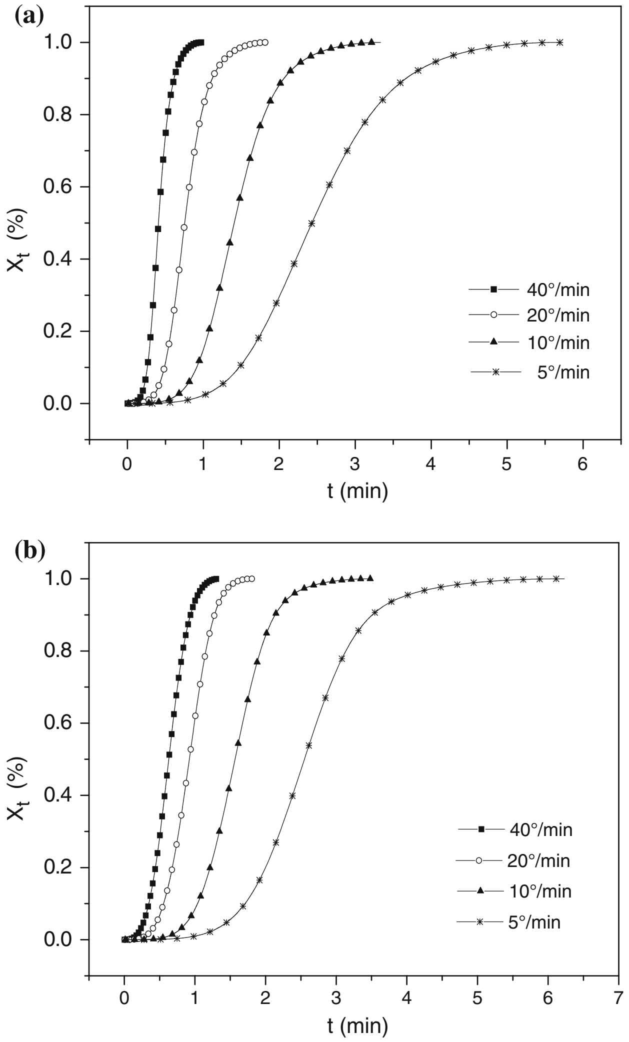

Fig. 4 X_t as a function of time for **a** PHBV, **b** PHBV70

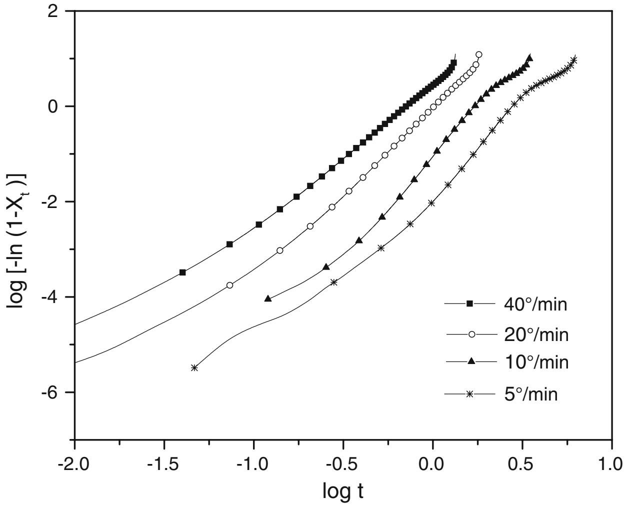

Fig. 5 Avrami plot of ln [−ln (1 − X_t)] versus ln t for PHBV70 polymer blend

constants [24], according to the relation $\log k_c = \frac{\log k}{\phi}$ (where ϕ is the cooling rate), are slightly different, and almost unchanged for all blends at certain cooling rate. The Avrami n parameter varies from 1.9 to 3. Similar values have been obtained for PHBV and PHBV/kenaf fiber composites [25].

Crystallization data were also analyzed by the Mo's model [26] based on both Avrami and Ozawa models. The well-known Mo's equation is given as $\log \phi = \log F(T) - a \log t$, where $F(T)$ refers to the value of the cooling rate, which is chosen at the unit crystallization time, when the measured system reached 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 the slope of the plots $\log \phi$ versus $\log t$ at different cooling rates. The characteristic plots of $\ln \phi$ versus $\ln t$, obtained by modified Mo's approach, are presented in Fig. 6. Linear correlations are obtained for each investigated system. The calculated $F(T)$ parameters,

Table 3 Parameters obtained from Avrami analysis and Jeziorny corrected constants for PHBV and its blends

ϕ (°/min)	PHBV			PHBV80			PHBV70			PHBV50		
	log k	n	k_c	log k	n	k_c	log k	n	k_c	log k	n	k_c
40	−0.58	2.1	0.96	−0.29	2.0	0.98	−0.54	2.1	0.96	−0.61	2.0	0.96
20	−0.99	2.3	0.89	−1.82	1.8	0.81	−1.25	2.2	0.86	−0.97	2.3	0.89
10	−2.22	1.5	0.58	−1.27	2.8	0.75	−2.65	1.5	0.54	−1.22	2.2	0.75
5	−1.72	3.0	0.45	−1.87	2.4	0.42	−2.34	2.3	0.34	−1.64	2.0	0.46

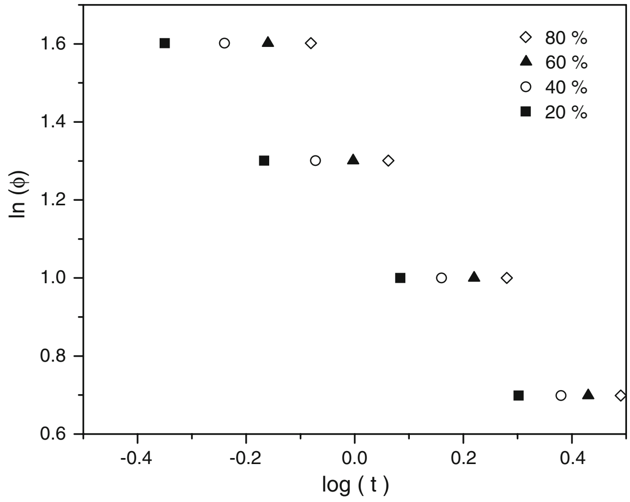

Fig. 6 Plots of log ϕ versus log t for PHBV70

Table 4 Values of a and $F(T)$ parameters versus X_t based on Mo treatment for PHBV and its blends with PDCHI

X_t (%)	PHBV		PHBV80		PHBV70		PHBV50	
	$F(T)$	a	$F(T)$	a	$F(T)$	a	$F(T)$	a
20	10.2	1.2	11.5	1.3	12.7	1.4	13.1	1.7
40	12.9	1.2	15.1	1.4	16.9	1.4	20.5	1.8
60	15.4	1.2	19.1	1.5	21.4	1.5	28.2	1.8
80	19.5	1.2	23.9	1.5	27.5	1.5	40.7	1.9

presented in Table 4, show that the $F(T)$ function increases with the increase of X_t. In polymer blends, this function has significantly higher value with the increase of PDCHI content for a certain X_t (20, 40 60, and 80%). This could be the evidence to show that the PDCHI content has significant influence on the crystallization kinetics. This is of course opposite to the results obtained from the Avrami approach, where the Jeziorny rate constants are almost independent of the second polymer content. It is evident that the Avrami equation is inadequate in the analysis of nonisothermal crystallization of polymers, since this model collects data related to low- and high-relative crystallization, while the Mo's analysis gives the crystallization functions related to certain X_t values.

Spectroscopic studies

Fourier transform infrared (FTIR) spectroscopy is used to study the formulation of PHBV/PDCHI blends. In many miscible blends, polymers containing carbonyl group usually undergo some interaction such as hydrogen bonding etc., and a shift of the band corresponding to the C=O group is observed.

FTIR spectrum, representative of PHBV, is shown in Fig. 7. A strong and sharp absorbance band at 1720 cm^{-1} could be assigned to the C=O stretching mode of the crystalline parts in PHBV. The small, almost invisible shoulder positioned at 1743 cm^{-1}, is also attributed to the same C=O stretching mode although it arises from the amorphous parts. In addition, the peaks at 1275, 1261, and 1226 cm^{-1} are assigned to the C–O–C stretching modes of the crystalline parts. The strong peak, detected near 1179 cm^{-1}, is attributed to the amorphous state of C–O–C stretching band [27]. Usually, the presence of the absorption bands above 3000 cm^{-1} are connected with the possibility of a C–H···O hydrogen bond [27, 28]. The weak shoulder, positioned at 3009 cm^{-1}, could be an evidence of C=O interacting with CH_3, which is in α position in the PHBV chain. Namely, it was considered that a chain of C–H···O hydrogen bond pairs link CH_3 in one helical structure and C=O group in other helical structure, which

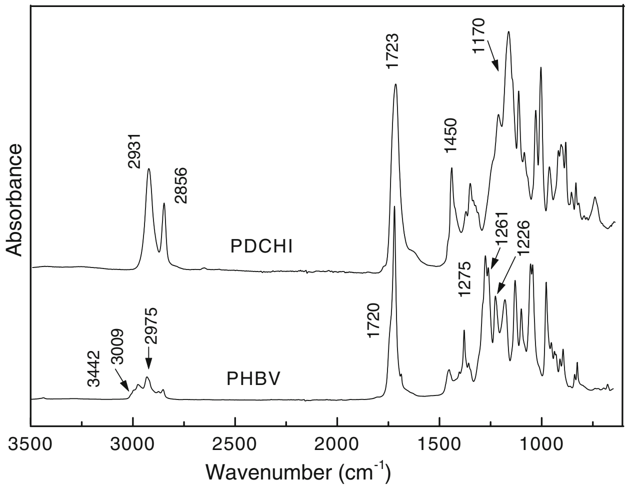

Fig. 7 FTIR spectra of PHBV and PDCHI films

are in anti-parallel orientation. The weak band at 3442 cm^{-1} is attributed to its hydroxyl end-groups [29].

The characteristic spectrum of PDCHI, also shown in Fig. 7, is characteristic for polyvinyl esters, and has an intensive band at 1723 cm^{-1}, ascribed to C=O stretching mode. The intensive bands at 2931 and 2856 cm^{-1} are due to C–H stretching (CH_2 groups present in vinyl chain as well as cyclohexyl rings). The strong band at 1170 cm^{-1} corresponds to C–O–C stretching, and the band at 1450 cm^{-1} is caused by the CH_2 bending characteristic for cycloalkanes.

The FTIR spectra of PHBV/PDCHI polymer blends (Fig. 8) show modified bands in shape and intensity when compared to those characteristics for neat polymers. Some bands that are crystalline sensitive peaks become weaker or disappear, depending on the blend composition. To analyze the real influence of the amorphous polyvinylester on crystalline PHBV, primarily the characteristic crystalline bands should be observed. It is interesting to note that the characteristic band for crystalline parts in PHBV, positioned at 1720 cm^{-1}, gradually decreases with the increase of PDCHI content (Fig. 9). In addition, it could be noted that the crystalline-sensitive peaks of PHBV at 1275, 1261, and 1226 cm^{-1} (C–O–C stretching mode) clearly become weaker in PHBV80 blend, while the first two peaks appear as almost invisible shoulders in PHBV70 and PHBV50 blends. The last band at 1226 cm^{-1} shifts to lower wave numbers and also shows significant decrease in intensity, depending of the PDCHI content. This result indicates that the crystallization of PHBV component is suppressed by the presence of bulky PDCHI content and the crystallinity is lower. These findings, and the changes in bands intensity and positions around 3000 cm^{-1}, could support the evidence that certain changes in crystallinity structure appear as a result of the crystallization process of PHBV. For example, the crystalline CH_3 band near 2995 cm^{-1}, present in the PHBV spectrum, completely disappeared in PHBV70 and PHBV50 blends. It is also important to note that the characteristic shoulder, responsible for C–H$\cdots$O hydrogen bond in two helical structures in the anti-parallel orientation in PHBV, is present only in the PHBV80 blend, while in the other two blends (PHBV70 and PHBV50) it completely disappears, probably due to the different position of the PHBV helical structure, influenced by the bulky cyclohexyl rings.

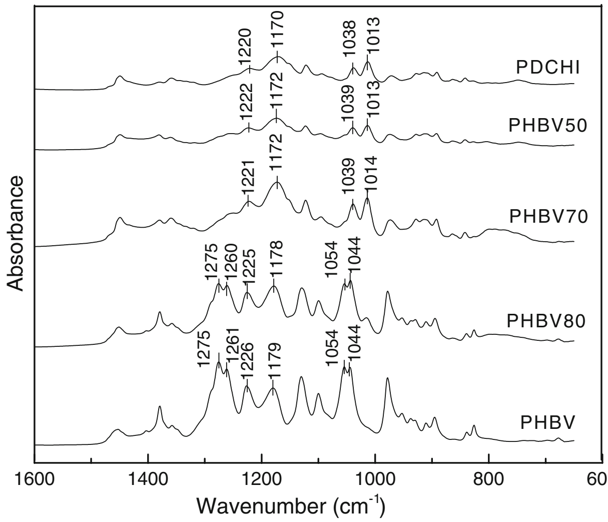

Fig. 8 FTIR spectra of the PHBV/PDCHI blends with different composition

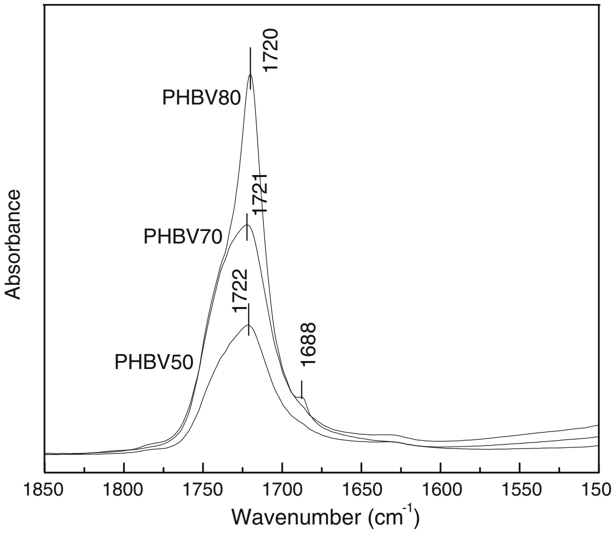

Fig. 9 FTIR spectra of PHBV/PDCHI blends with different composition in the carbonyl region

That this is really the case is also confirmed by the intensity increase of the band near 1179 cm^{-1}. This peak was ascribed to the amorphous state of C–O–C stretching band, and its shifting to lower wave numbers with the increase of PDCHI content. This intensity increase implies that the amorphous phase of PHBV component in the blend increases. The fixed position of 1720 cm^{-1} band without any shifting, with the absence of any new bands around 1700 cm^{-1}, is another evidence that the C=O group in PHBV is not involved in the formation of any intermolecular hydrogen bonds. From this point of view, the PHBV/PDCHI systems could be identified as immiscible.

Hydrolytic degradation

Figure 10 shows the weight loss of PHBV and its blends as a function of exposed time in alkaline solutions. It is obvious that PHBV50 blend has almost the same degradation trend as PHBV film, while for the other two polymer blend films (PHBV80 and PHBV70) the hydrolytic degradation unexpectedly proceeded considerably slower. As

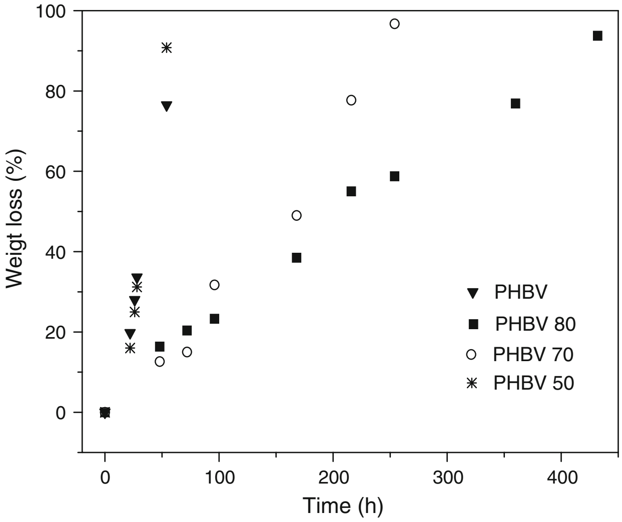

Fig. 10 Weight loss of PHBV/PDCHI films during the hydrolytic degradation in 1 NaOH

the thickness of polymer films was quite identical, this behavior might suggest that certain changes in PHBV crystal structure obviously happened. Since an almost linear trend between the weight loss and exposed time could be observed, the hydrolytic degradation rate could be defined as a slope of the plots presented in Fig. 10. The hydrolytic degradation rates of 1.7, 1.2, 0.25, and 0.16, expressed as weight loss in percentage per hour (%/h) for PHBV, PHBV50, PHBV70, and PHBV80, respectively, clearly show that degradation rate could be widely controlled by the second polymer content. To clarify this behavior, further morphological tests will need to be carried out.

Conclusions

The thermal and kinetic properties related to the nonisothermal crystallization of PHBV blended with PDCHI have been analyzed, depending on PDCHI content.

Thermal analysis of PHBV/PDCHI blends showed that the presence of bulky PDCHI reduces the crystallinity of PHBV at PDCHI content higher than 70 wt%. The kinetic properties related to nonisothermal crystallization from the melt, analyzed by Mo's model, have shown that the rate of crystallization of PHBV is significantly suppressed by the increase of PDCHI content. In alkaline solution, the hydrolytic degradation of polymer blends containing 20 and 30 wt% of PDCHI proceeded considerably slower compared to the pure PHBV.

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References

1. Mohanty AK, Misra M, Drzal LT (2002) J Polym Environ 10:19
2. Mwaikamo LY (2004) In: Tucker N, Johnson M (eds) Low environmental impact polymers. Rapra Technology, Shawbury, UK, p 1
3. Yu L, Dean K, Li L (2006) Prog Polym Sci 31:576
4. Ha CS, Cho WJ (2002) Prog Polym Sci 27:759
5. Doi Y (1990) Microbial polyesters. VCH, New York
6. Avella M, Martuscelli E, Raimo M (2000) J Mater Sci 35:523. doi:10.1023/A:1004740522751
7. Buzarovska A, Bogoeva-Gaceva G, Grozdanov A, Avella M (2006) J Appl Polym Sci 102:804
8. Bogoeva-Gaceva G, Avella M, Malinconico M, Buzarovska A, Grozdanov A, Gentile G, Errico ME (2007) Polym Composites 28:98
9. Avella M, Bogoeva-Gaceva G, Buzarovska A, Errico ME, Gentile G, Grozdanov A (2007) J Appl Polym Sci 104:3192
10. Shanks RA, Hodzic A, Wong S (2004) J Appl Polym Sci 91:4
11. Avella M, La Rota G, Martuscelli E, Raimo M, Sadocco P, Elegir G, Riva R (2000) J Mater Sci 35:829. doi:10.1023/A:1004773603516
12. Wong S, Shanks R, Hodzic A (2002) Macromol Mater Eng 287:647
13. Maiti P, Batt C, Giannelis EP (2007) Biomacromolecules 8:3393
14. Koyama N, Doi Y (1997) Polymer 38:1589
15. Shirahase T, Komatsu Y, Tominaga Y, Asai S, Sumita M (2006) Polymer 47:4839
16. Silvestre C, Cimmino S, Di Pace E, Martuscelli E, Monaco M, Buzarovska A, Koseva S (1996) Polym Networks Blends 6:73
17. Scandola M, Focarete ML, Adamus G, Sikorska W, Baranovska I, Swierczek S, Gnatowski M, Kowalczuk M, Jedlinski Z (1997) Macromolecules 30:2568
18. Buzarovska A, Koseva S, Cvetkovska M, Nedkov E (2001) Eur Polym J 37:141
19. Organ SJ, Barham PJ (1991) J Mater Sci 26:1368. doi:10.1007/BF00544479
20. Patel RM, Bheda JH, Spruiell J (1991) J Appl Sci 42:1671
21. Avrami MJ (1939) J Chem Phys 7:1103
22. Avrami MJ (1940) J Chem Phys 8:212
23. Avrami MJ (1941) J Chem Phys 9:177
24. Jeziorny A (1978) Polymer 19:1142
25. Buzarovska A, Bogoeva-Gaceva G, Grozdanov A, Avella M, Gentile G, Errico M (2007) J Mater Sci 42:6501. doi:10.1007/s10853-007-1527-8
26. Liu T, Mo Z, Wang S, Zhang H (1997) Polym Eng Sci 37:568
27. Sato H, Murakami R, Padermshoke A, Hirose F, Senda K, Noda I et al (2004) Macromolecules 37:7203
28. Matsuura H, Yoshida H, Hieda M, Yumanaka S, Harada T, Shin-ya K (2003) J Am Chem Soc 125:13910
29. Gao Y, Kong L, Zhang L, Gong Y, Chen G, Zhao N, Zhang X (2006) Eur Polym J 42:764