

Thermogravimetry of Poly(beta-hydroxybutyrate) and its Blends with Polypropylene and Poly(methyl methacrylate)

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Received: 4 September 1994; accepted 6 March 1995

ABSTRACT

Decomposition of biologically prepared poly(beta-hydroxybutyrate) into volatile products is slightly affected when nonisothermal experiments are carried out in air instead of nitrogen. The process of decomposition of PHB into volatile products is influenced by molecular mass of the polymer within the range 8,390 - 539,000, with medium molecular masses being the most stable. A melt behaviour of PHB is demonstrated by a gradual change of endotherms of melting of PHB which splits into three peaks with simultaneous shift of temperature of their maximum to lower values. It is ascertained that residual amounts of PHB decomposition affect the subsequent decomposition of PP, PE and PMMA into volatiles, the effect on polypropylene being the most pronounced. A significant back effect of second polymer on decomposition of PHB in its blends is observed for the case of poly(methyl methacrylate).

Key Words: poly(beta-hydroxybutyrate), thermogravimetry, nonisothermal and isothermal, decomposition, blends

INTRODUCTION

Poly(beta-hydroxybutyrate) (PHB) is a thermally unstable aliphatic polyester and degrades quite quickly when it melts [1]. The stabilization of this polymer against thermal degradation during its melt processing is a challenge to investigation efforts aimed at the more practical applications of PHB.

In this work an attempt has been made to

study the decomposition of PHB with different molecular mass into volatile products by nonisothermal and isothermal thermogravimetry (TG). The changes in the melt stability were examined by DSC. To improve the melt stability of PHB it was found necessary to ascertain whether other polymers such as polyethylene, polypropylene and poly(methyl methacrylate) affect the decomposition of PHB into volatile products and vice versa. The nonisothermal

thermogravimetry curves of blends of PHB with these polymers were analyzed as being composed of two independent temperature dependent processes of formation of volatile products. Such an evaluation of thermal stability of polymers and the blends of polymers was introduced earlier [2,3] and was found useful for the characterization of "volatilization" of several independent components of the polymer system.

EXPERIMENTAL

Materials

PE used was Marlex 5580, a product of Phillips Chem. Company, USA, and was free of inhibitors with melt flow index of 8, and density 0.955 g/cm^3 ; PMMA was a Rohm/Haas 8 N atactic product, with a $T_g=105^\circ\text{C}$; PP (isotactic) of Tatren TF 411 was a product of Slovnaft Bratislava, Slovakia. All polymers were free of stabilizers. PHB (homopolymer) high purity powder was supplied by Marlborough Biopolymers, England in three grades:

BX GO8	M.W. 539,000
BX AMC 2/1	M.W. 73,600
BX IC T/9/1-25	M.W. 8,390

Sample Preparation

The polymer powders were mixed mechanically, and the polymer blend was kept at 200°C for 15 minutes in TG apparatus (Perkin-Elmer TGS 1) to acquire an equilibrium in the melt and then heated at 10 K/min . The flow of nitrogen was 6 L/h .

DSC measurements were carried out on Perkin Elmer DSC 2 equipment according to conditions discussed in the text.

RESULTS AND DISCUSSION

Nonisothermal thermogravimetry curves of degradation of three PHB samples in nitrogen can be seen in Figure 1.

The highest molecular mass 539,000 is the

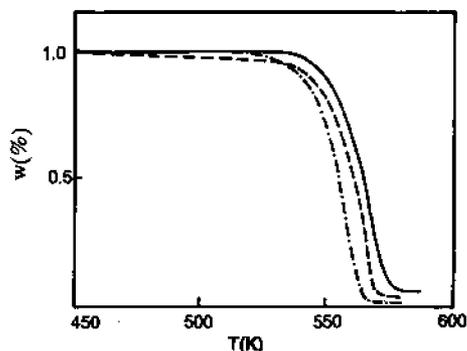


Figure 1. Nonisothermal thermogravimetry records of PHB samples in nitrogen (rate of heating = 10 K/min and initial mass of sample = 2 mg).

Molecular mass of PHB = 73,600 ——— 8,390 - - -
539,000 ·····

least stable; the highest stability was observed for the molecular mass 73,600, the difference between 539,000 and 73,600 samples is not, however, very large. According to data of Table 1, the rate of formation of volatile products from PHB of highest molecular mass in air is slower than that for PHB in nitrogen while the opposite is true for PHB of medium molecular mass. It is difficult to ascribe the rather high values of apparent activation energy (Table 2) i.e. values higher than 300 kJ/mol , for termination order $m=1$ [2] to a specific chemical degradation process.

This is an indication that the abrupt evaporation of degradation products takes place in

Table 1. Residual mass w of PHB samples at 550 K (the rate of heating 10 K/min , initial amount of sample 2 mg).

Atmosphere	Molecular mass of PHB	w
Nitrogen	539,000	0.717
	73,600	0.909
	8,390	0.824
Air	539,000	0.808
	73,600	0.864
	8,390	0.837

Table 2. Apparent activation energy E and preexponential factor $\ln A/\beta$ (β is the rate of heating) determined from one-component nonisothermal TG records of individual samples of PHB for formal termination order $m=1$ and $m=0.5$.

Atmosphere	M.W. of PHB	E (kJ/mol)		$\ln A/\beta$	
		$m=1$	$m=0.5$	$m=1$	$m=0.5$
Nitrogen	8,390	309	204	63.2	41.1
	73,600	394	229	72.2	46.3
	539,000	336	225	70.5	46.2
Air	8,390	332	222	68.8	45.1
	73,600	317	213	65.2	43.0
	539,000	330	222	68.5	45.1

the sample following their continuous accumulation until some critical value of lower molecular mass is attained. In such a case it is proved that the order of termination, $m=0.5$, [4] leads to a better approximation of the process showing that the most of the active particles of the polymer degradation are lost by evaporation. Activation energy for the formation of volatile products estimated for $m=0.5$, is 220 kJ/mol which appears to be a reasonable value for such a process; 247 ± 19 kJ/mol was reported for the chain scission process [1].

More significant differentiation of the tendency of respective molecular masses of PHB towards decomposition into volatile products can be obtained from isothermal TG experiments in nitrogen atmosphere (Figures 2, 3).

The curves of the weight loss versus time for different molecular masses at 260°C show distinctly that the least stable sample is that with the highest molecular mass while the most stable is the sample of medium molecular mass. It may be seen that after 10 minutes at 260°C , the residual relative weight of sample of molecular mass 73,600 is 0.885, that of molecular mass 8,390-0.825 and molecular mass 539,000-0.36, respectively. The model taking into account the termination of active centres on the surface of decomposed polymer used for the interpretation of mass (w)-versus time (t) curves has the following analytical shape [4]:

$$w = 1 - (1 - e^{-kt})^{1/m} \quad (1)$$

where k is the rate constant of chain scission and m

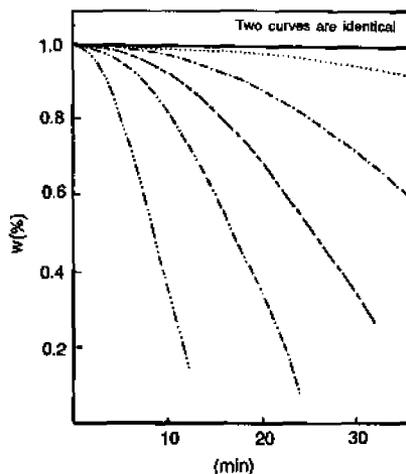


Figure 2. Isothermal thermogravimetry records of PHB of molecular mass 539,000 (initial mass of sample=2 mg).
 260°C ; - · - · - 250°C ; - - - 240°C ; — 230°C ;
 - - - - 220°C ; — — — 210°C ; — 200°C

is the formal order of termination. For evaluation of nonisothermal curves $m=0.5$ and 1 were used as the average values.

For isothermal thermogravimetry experiments, the values k and m were optimized from experimental curves using the equation 1 for each temperature. The results are summarized in the Table 3.

The rate constant k of chain scissions increases with temperature, while the formal order m of termination decreases. The data of Table 3

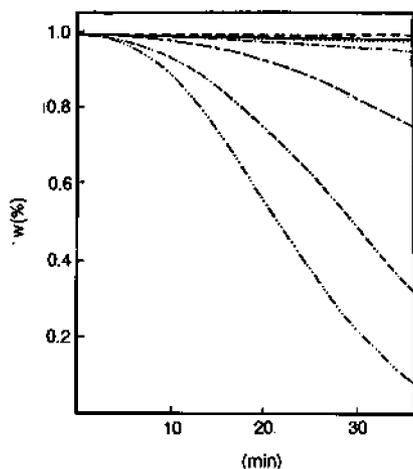


Figure 3. Isothermal thermogravimetry records of PHB of molecular mass 73,600 (initial mass of sample=2 mg).

..... 280 °C; · · · · · 250 °C; - - - - - 240 °C; — 230 °C;
 - · - · - 220 °C; — · — · 210 °C; - - - - - 200 °C

partially reveal the particular position of medium molecular mass 73,600 on the stability scale. The rate constant k of chain scission decreases with decreasing molecular mass while termination order m increases. At the same time, order of termination indicates how the volatiles are being formed from the site of a primary scission; the higher the order of termination (the lower rate of termination), the higher the probability of decay of

active centres of polymer degradation at the site of the primary degradation attack and the less abrupt volatilization of the sample occurs. Activation energy of bond scissions determined from isothermal values of k is 218 kJ/mol for sample of molecular mass 539,000, and 260 kJ/mol for molecular mass 73,600 and finally 352 kJ/mol for low molecular mass 8,390.

Nonisothermal Thermogravimetry of PHB Blends

Representative runs of decomposition of PHB of molecular mass 73,600 blended with PE are illustrated in Figure 4.

In nonisothermal curves, a well distinguished part belonging to the volatilization of PHB itself and that of the second polymer of a blend can be seen. When using the procedure of separation of partial processes corresponding to volatilization of two independent components as proposed before [3], we obtain the following values of activation energy and preexponential factor (Table 4).

Here, we assume that decomposition of each polymer occurs according to the formal scheme of the first order corresponding to the formal order of termination $m=1$. It was shown before [2] that when no interactions exist between two compounds (physical or chemical) of the blend, then the activation energy related to the decomposition of each component should remain constant independently of the composition of the blend. Such a case is, however, the ideal one. As it was already pointed out for blends of PP/PE,

Table 3. The values of k and m of isothermal decomposition of PHB samples.

Temperature (°C)	Molecular mass of PHB					
	539,000		73,600		8,390	
	m	k min	m	k min	m	k min
260	0.165	1.62	0.178	0.58	0.229	0.43
250	0.126	1.21	0.250	0.28	0.375	0.20
240	0.190	0.44	0.380	0.06	0.649	0.02
230	0.248	0.18	-	-	-	-
220	0.400	0.03	-	-	-	-
	E=218 kJ/mol		E=260 kJ/mol		E=352 kJ/mol	

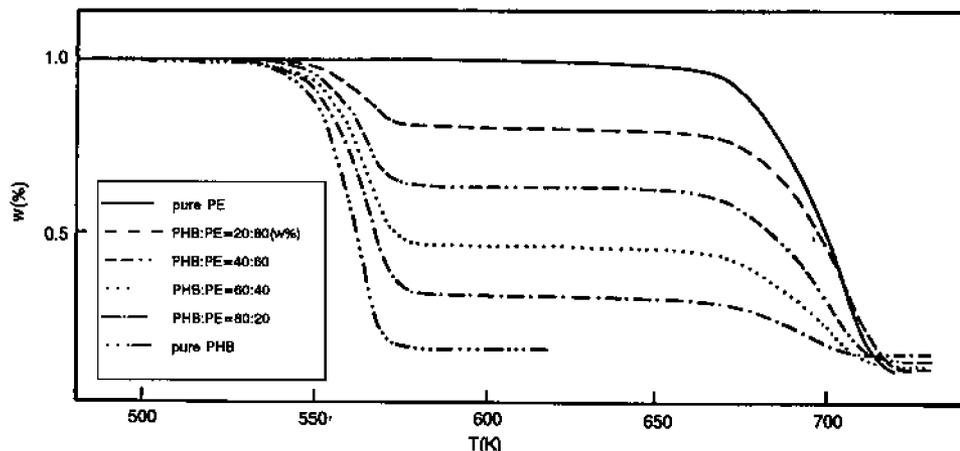
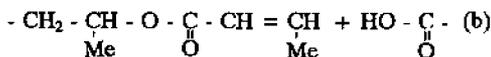
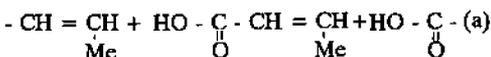
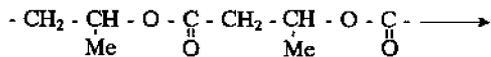


Figure 4. Nonisothermal TG curves of blends of PHB (73,600) + PE in nitrogen (rate of heating = 10 K/min and initial mass of sample = 2 mg).

PP/PMMA and PE/PMMA, a less stable component affects the decomposition of a more stable component and vice versa [3].

For the blends of PHB with these polymers the former probably decomposes via cyclic mechanism reported before [1], and schematically depicted as:



where either one molecule of crotonic acid at each chain scission (scheme a) or two macromolecular fragments (scheme b) are formed. From the Figure 4 it may be seen that almost all PHB is "volatilized" when the decomposition of the second polymer starts. It is therefore surprising that still some effect on activation energy of polymer decomposition exists (Table 4). Apparently it seems as if the residual amounts of the char (13% of initial mass) formed in decomposition of PHB play some role in termination reaction of the decomposing

second polymer. The most pronounced reduction of apparent activation energy can be observed for 1:1 initial mass of both polymers in the case of PP (Figure 5).

Apparent activation energy of PHB decomposition decreases significantly with the content of PHB in the blend with PMMA, in the case of other polymers the reduction is within 10 kJ/mol.

Even in the blends, the sequence of stability of PHB with different molecular masses is $73,600 \geq 539,000 > 8,360$, which corresponds to that found for pure polymers.

DSC Evaluation of Melt Stability

Each molecular mass of PHB was subjected to heat up to a temperature 470 K with the rate of 10 K/min., during which the melting endotherm was recorded; at this temperature, the polymer was kept for 40 minutes and then the sample was cooled (at the rate 10 K/min.) to room temperature. This cycle was repeated several times. After such a procedure, the melting endotherm splits into three peaks and temperature of the maximum rate of heat absorption shifts to lower values (Figure 6, Table 5).

Overall heat of fusion, corresponding to the

Table 4. The parameters determined from nonisothermal thermogravimetry analysis of blends of PHB with PP, PE and PMMA (rate of heating = 10 K/min).

Mol mass of PHB	Initial weight of PHB : PP	E ₁ kJ/mol	E ₂ kJ/mol	lnA ₁ /β	lnA ₂ /β	α ₁	α ₂
PHB + PP							
8,360	80 : 20	299	218	61.7	37.0	0.74	0.19
	60 : 40	301	161	62.0	26.5	0.55	0.30
	40 : 60	296	175	60.9	28.9	0.40	0.60
	20 : 80	293	182	60.1	29.9	0.20	0.79
73,600	80 : 20	355	158	73.8	26.5	0.70	0.17
	60 : 40	335	92	69.5	12.2	0.53	0.42
	40 : 60	344	166	71.4	27.1	0.35	0.61
539,000	80 : 20	324	189	68.4	32.3	0.72	0.20
	60 : 40	323	169	67.9	27.9	0.55	0.41
	40 : 60	316	185	66.2	30.9	0.38	0.60
	20 : 80	303	178	63.8	29.2	0.19	0.81
PHB + PE							
8,390	60 : 40	306	269	63.2	43.2	0.54	0.37
	40 : 60	301	309	62.2	50.2	0.35	0.55
73,600	80 : 20	341	326	70.6	54.2	0.69	0.17
	60 : 40	346	306	71.7	50.2	0.54	0.35
	40 : 60	344	316	71.4	51.9	0.37	0.51
	20 : 80	335	349	69.4	57.2	0.20	0.71
539,000	80 : 20	324	239	67.9	38.7	0.69	0.19
	60 : 40	321	222	67.5	35.6	0.53	0.36
	40 : 60	317	246	66.6	39.5	0.36	0.56
	20 : 80	318	322	67.1	52.7	0.19	0.74
PHB+PMMA							
8,390	80 : 20	288	259	59.3	46.9	0.74	0.15
	60 : 40	263	239	53.4	43.0	0.60	0.28
	40 : 60	249	220	50.3	38.9	0.45	0.46
	20 : 80	210	231	41.9	41.2	0.25	0.66
73,600	80 : 20	327	223	67.9	39.8	0.73	0.16
	60 : 40	292	186	59.8	32.7	0.57	0.32
	40 : 60	266	198	54.2	34.8	0.41	0.47
539,000	80 : 20	313	208	65.7	36.7	0.69	0.10
	60 : 40	295	213	62.0	37.7	0.51	0.35
	40 : 60	272	202	56.6	35.5	0.35	0.52
	20 : 80	239	201	49.3	35.3	0.19	0.69

E₁ is an apparent activation energy of PHB decomposition; E₂ is an apparent activation energy of second component of a blend decomposition (PP, PE, PMMA).

lnA₁/β, lnA₂/β are preexponential factors; α₁, α₂ are fractions corresponding to each component of a blend.

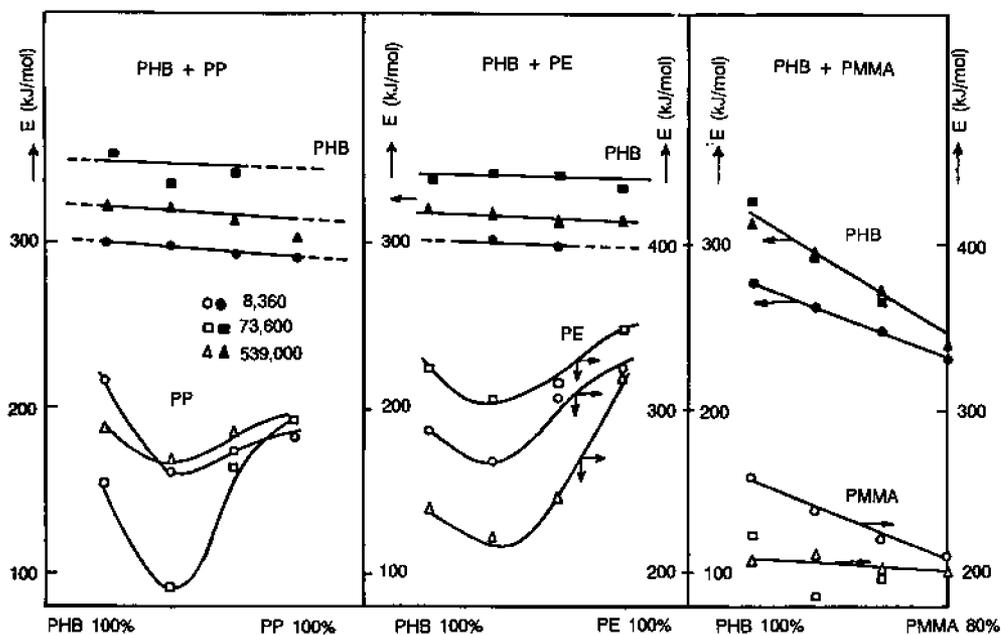


Figure 5. The plot of apparent activation energy E of decomposition of respective component of a PHB blend with PP, PE and PMMA on the composition of the blend.

(formal kinetic order of decomposition was 1).

Table 5. Parameters of endotherms of melting of PHB samples in repeated cycles of heating up to 470 K, 40 minutes of sample standing at this temperature and cooling to room temperature.

Sample mol.mass	Cycle no	T_{1max} K	v_{1max} J/gs	ΔH_1 J/g	T_{2max} K	v_{2max} J/gs	T_{3max} K	v_{3max} J/gs
8,390	1	424.5	1.28	99.9				
	2	412	1.02		401	0.79	383	0.37
	3	401	0.59		382	0.35	362	0.15
73,600	1	440.5	1.83	91.4				
	2	431	2.09				417	0.48
	3	423	1.51				407	0.40
	4	421	1.16		414	1.09	397	0.48
539,000	1	446.5	1.49	78.9				
	2	427	1.55				410	0.36
	3	412	0.83		399	0.51	379	0.149

$T_{i max}$ - temperature of the maximum of the i -th endotherm.

$v_{i max}$ - rate of heat absorption at $T_{i max}$. ΔH_1 - heat corresponding to the first endotherm.

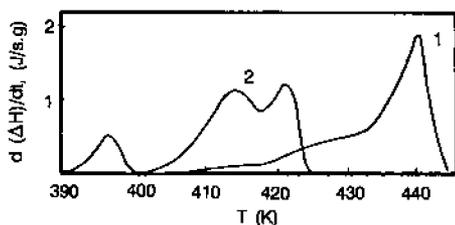
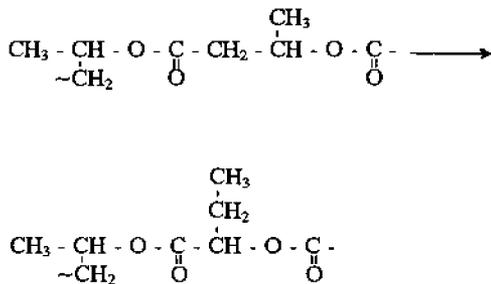


Figure 6. Endotherms of melting of PHB (73,600) at first (1) and fourth (2) melting-cooling cycle.

The rate of heating and cooling=10 K/min. In each cycle, the sample was kept at 470 K for 40 minutes. The initial mass of sample=3 mg.

first melting, decreases with the molecular mass of the sample. According to reference 1 the melting temperature of a pure PHB at 451-453 K and heat of fusion about 110 kJ/g were found, respectively. Onsets of the endotherms of pure PHB [1] are at 437 K while in our report they indicate 385, 406 and 419 K for molecular masses 8,390, 73,600 and 539,000 respectively.



The endotherms of our samples are considerably broader, and the temperature interval from the start of endotherm to its maximum being 39.5, 34.5 and 27.5 K for molecular masses 8,390, 73,600 and 539,000, respectively, while 14 K only was reported in reference 1. An interesting discrepancy was presented by these authors namely that synthetically prepared polylacton, which mimics the biologically prepared PHB, is much more stable according to MFI stability test while

the opposite behaviour was observed when comparing data of chain scission determined by GPC. Within possible explanations, the one based on the intramolecular rearrangement of beta-hydroxybutyrate units of biologically prepared PHB into alpha-hydroxybutyrate units occurring in the polymer melt appears to be the most promising.

The melting temperature of PHB containing poly(alpha-hydroxybutyrate) units should be reduced as well as heat of polymer fusion. Such a speculation is in agreement with the nonisothermal thermogravimetry experiments on pure PHB where volatiles from the polymer are released in a rather narrow temperature interval from a higher molecular weight precursor. Also, the boiling temperature (189 °C) of crotonic acid which appears to be the only low molecular product being formed at each chain scission and the fact that weight loss after 40 minutes of heat treatment of 73,600 sample at 200 °C was lower than 1%, (Figure 2) indicates that some intramolecular rearrangement in a polymer before its complete destruction takes place.

CONCLUSION

The reasonable values of activation energy of PHB decomposition into volatile products as investigated by both the isothermal and nonisothermal thermogravimetry can be obtained only when the process of termination of reactive moieties, through which the "volatilization" of PHB occurs becomes less significant. This is expressed in the values of the termination order lower than 1 indicating the extent of the passage of the reactive species into the gaseous phase without the chemical reaction.

The decomposition of PHB in blends with PP, PE and PMMA is affected mainly by the presence of PMMA. At the same time PHB affects more the decomposition of PP and PE into volatiles than that of PMMA. The melt instability demonstrated by a gradual transformation of DSC endotherms into several peaks after repeating melting-freezing cycles requires the further study

from the viewpoint of possible stabilization strategies.

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