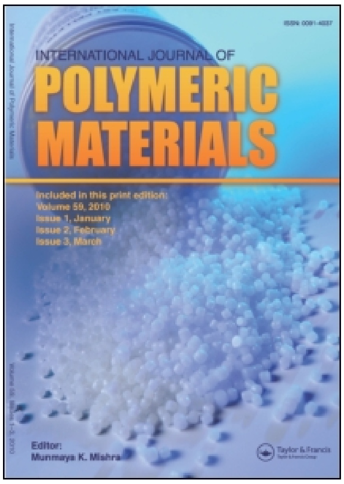

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Poly(hydroxybutyrate-co-hydroxyvalerate)-polyadipate blends

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POLY(HYDROXYBUTYRATE-co-HYDROXYVALERATE) – POLYADIPATE BLENDS

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Poly(β-hydroxybutyrate) (PHB) and its copolymers (P(HB-co-HV)) are biocompatible 'green' thermoplastics. These polymers would be in widespread use if it were not for their high price. One method of reducing this price is by blending it with another, less expensive, material while retaining or improving its desirable properties. Poly(hydroxybutyrate-co-hydroxyvalerate) (P(HB-co-HV)) – polyadipate (PEA) blends were studied. DMA and DSC experiments were used. The thermal analysis indicates that these blends are miscible until close to 30 wt% polyadipate content. The study of the blend crystallinity was carried out by the isothermal melt of the blend. The crystallization process has a induction time. The addition of polyadipate (less than a 30 wt%) decreases the induction time. As consequence, PEA can be used as nucleating agent for the crystallization of P(HB-co-HV). The mechanical properties and the thermal decomposition were studied too. The elastic modulus and the activation energy of the thermal decomposition decrease with PEA addition.

Keywords: crystallization, polyhydroxyalkanoates, polyadipate, blends, nucleating agents

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INTRODUCTION

Poly(β-hydroxybutyrate) (PHB) and their copolymers (P(HB-co-HV)) are biocompatible ‘green’ thermoplastics [1] and biodegradable in specific treatment system. There is little doubt that these polymers would be in widespread use if it were not for their high price. One method of reducing this price is by blending it with another, less expensive, material while retaining or improving its desirable properties [2].

This polymer family, polyhydroxyalkanoates, (PHA), are highly semi-crystalline polyesters. They are very brittle and have poor processability.

Crystallization behavior of these polymers has been extensively studied [3–6], however, many experimental and theoretical questions are still unsolved due to the complexity of the nucleation and growth phenomena of macromolecular crystals of PHB. The melting history can modify the polymer structure due to mechanical crosslinking or degradation phenomena.

Compared with other thermoplastics, the nucleation density of these polymers is relatively low, leading to slow crystallization rates. This low nucleation density means that it is possible to grow spherulites several mm in diameter by crystallization from the melt. This fact affects the mechanical properties of the polymer because this material is more brittle as the spherulite is larger in diameter. Also, the low nucleation density achievable through homogeneous nucleation leads to excessively long cycle time in fabrication processes such as injection molding. This potential problem can be overcome, using nucleating systems.

The study of the crystallization phenomena is of great importance in polymer processing, for several reasons. The control of temperature profile during cooling, in the final stage of a process, determines the development of a specific morphology, which influences the final properties of the material. Modeling of isothermal crystallization gives information on kinetics and morphology developed at each crystallization temperature. In the macro-kinetics approach, the dependence of the degree of crystallization on time and temperature must be defined in order to model and optimize the final crystallinity structure of the polymer.

In this paper, blending of P(HB-co-HV) with polyethylene adipate (PEA) was studied. The second polymer is amorphous and a known plasticizer. Characteristics of polymer blend as miscibility, crystallinity, mechanical properties and thermal decomposition, were studied.

Experimental

Materials

P(HB-co-11%HV) supplied by Aldrich Chemical Co. ($\bar{M}n = 150\,000$) was used. The polyethylene adipate (PEA) consist of polyester based on adipic acid with diols (ethylene and diethylene). Commercial ester was available from Norenplast Company ($\bar{M}n = 2\,000$).

Chemical Structure of PEA

The ^{13}C NMR was used for the chemical structure study. The NMR measurements were carried out at 300 K using a Brucker AC 250 F spectrometer at 250 MHz (^{1}H) and 62.9 MHz (^{13}C). Samples were analyzed in 5 mm sample tubes in chloroform-d. The spectra were referenced to internal TMS.

Sample Preparation

The films were prepared by casting of chloroform solution at room temperature on a plane Pyrex surface. Then, it was kept during 15 days at room temperature to achieve full crystallization.

DSC Experiments

A Dupont 990 Thermal Analyzer was used for the calorimetric study. Sample mass was 5 – 10 mg. Isothermal crystallization was performed under nitrogen atmospher on the following schedule: samples were heated from 25°C to 180°C at 10°C/min, kept at this temperature for 10 min and quenched with dry ice. After quenching, they were immediately placed into the DSC, preset to crystallization temperature. Isothermal runs were performed until the crystallization peak reached the base line. Crystallization temperatures were changed from 40 to 100°C. Immediately after the isothermal run, a dynamic run at 10°C/min was performed in the crystallized sample and T_m was measured at the peak of fusion.

DM4 Experiments

Dynamical mechanical test were carried out in the glass-rubber transition temperature range with a Perkin-Elmer 7-e Series Thermal Analysis System, working in extension mode. Dynamic and static stress were 2.5×10^5 Pa and 3.5×10^5 Pa, respectively. The specimen was a thin film with dimensions 15 mm × 5 mm × 0.2 mm. Measurements were performed at 10 Hz between – 110°C and 100°C.

Mechanical Properties

Theses properties were measured in an Instrom 4467 testing machine with uniaxial tensile test at room temperature. Measurements were made at crosshead speed of 10 mm/min. Three run of each material were done. Tensile modulus, E, was calculated form the initial slope of the stress-strain plot.

Thermal Decomposition

The study was carried out in Mettler TA 4000 Thermogravimeter at a heating rate of 10°C/min under nitrogen atmosphere. The weight of the sample was 3 – 7 mg, temperature range 25 – 500°C.

RESULTS AND DISCUSSION

Chemical Structure of PEA

Two structures are present in the polyeser (Fig. 1): 1.-chains with diethylene ether (II), or 2.-chains with ethylene group (I), between ester groups. The relative quantity of one group to the other (II/I) was obtained by NMR measurements. Figure 2 shows the ^{13}C spectrum of the sample and Table 1 shows the assignment of the chemical shifts for carbon which are in agreement with the calculated chemical shifts, using data from tables. The relative quantity (II/I = I (k, l)/I(g, h) = 1.28, then there is % 55 of II structure.

Miscibility of the Blends

Thermal characterization of polymer blends is a well known method for determining their miscibility. P(HB-co-11%HV) – PEA blends were studied by DSC and DMA.

Theses blends show a single Tg value (Tab. 2). The PEA glass transition temperature was measured by DSC and it was $-60°C$. Blend Tg are lower than those of PHA and higher than PEA. In amorphous and miscible blend, Tg is equal to the volume fraction average of the Tg of the component polymers ($Tg = \Sigma\phi_i \, Tg_i$) [7]. Table 2 shows experimental and calculated Tg values. These values are not in good agreement, because PHA is a semicrystalline polymer, but they are between the Tg value of the two polymers.

A miscible blend containing a semicrystalline polymer possesses two important characteristics in addition to the single Tg of the mixed amorphous phase [2]. The first characteristic is that a change is observed in the crystallization behavior of the semicrystalline polymer. A change is observed in the

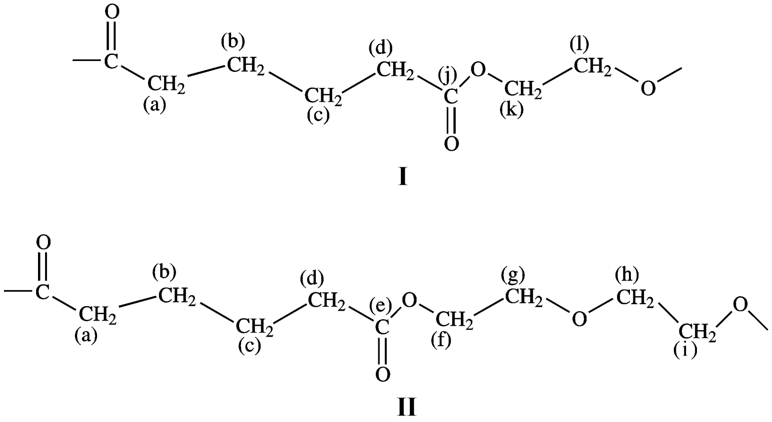

FIGURE 1 Chemical structures of PEA.

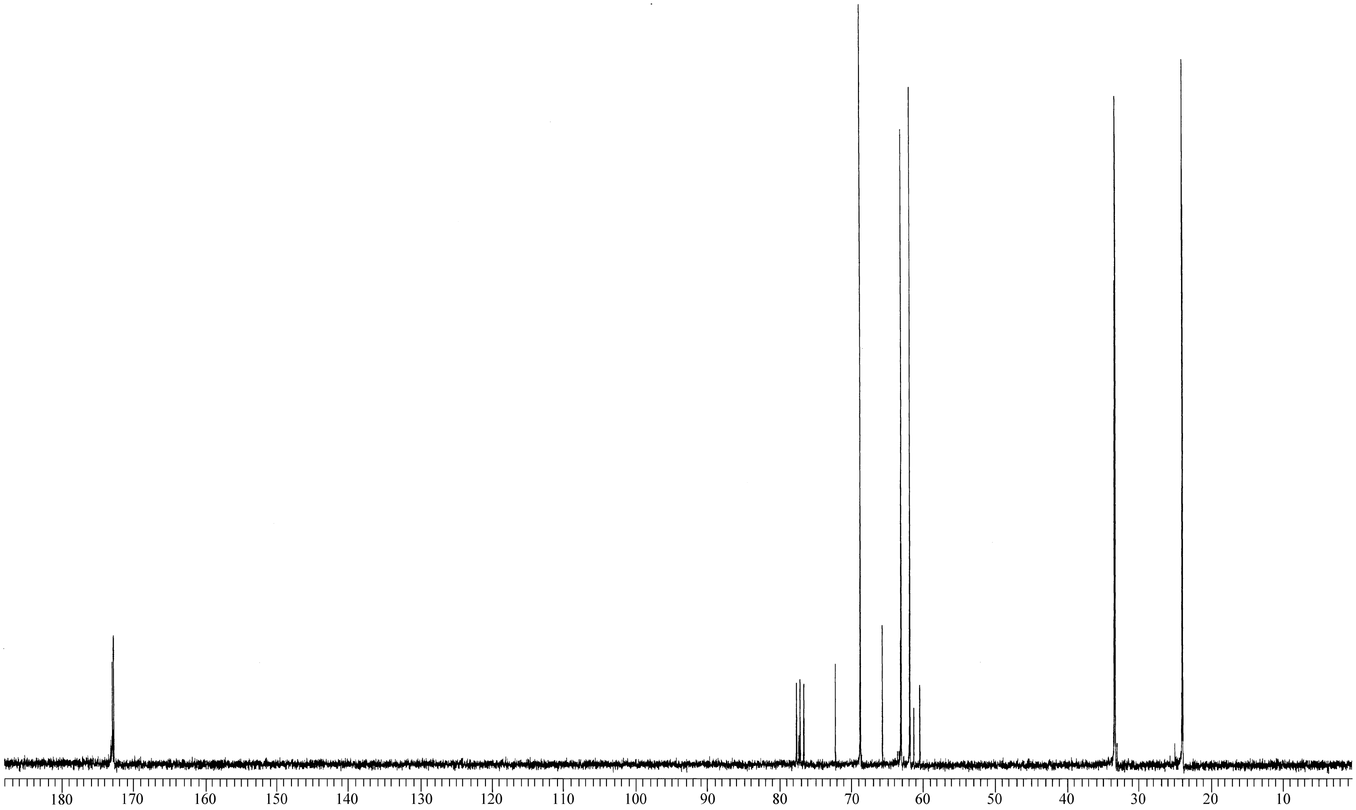

FIGURE 2 ^{13}C NMR spectrum of PEA.

TABLE 1 ^{13}C NMR experimental data

Carbon	*Signal* (*ppm*)
a, d	33.24
b, c	23.86
e	173.05
f, i	62.96
g, h	68.67
j	172.6
k, l	61.7

TABLE 2 Tg values of the DMA experiments

Samples	*Tg* (°*C*) (*calculated*)	*Tg* (°*C*) *E″*
P(HB-co-11%HV)	–	−8
P(HB-co-11%HV)-5%PEA	−11	−12
P(HB-co-11%HV)-10%PEA	−17	−11
P(HB-co-11%HV)-30%PEA	−24	−10
P(HB-co-11%HV)-50%PEA	–	−8

growth rate of spherulites when a miscible polymer constituent is added. The crystallization rate is higher if the Tg of the blend is lower than that of crystallizable polymer. Figure 3 shows this effect in P(HB-co-11%HV)/PEA blend samples of different composition as is expected because the resultant blend Tg is lower than that of the crystallizable polymer.

Addition of an amorphous polymer to semicrystalline polymer results in a decrease in overall crystallinity of the blend [2]. Table 3 shows this behavior.

The other characteristic demostrating miscibility of blends containing a semicrystalline polymer is the depression of the equilibrium melting point of the polymer when an amorphous one is present [2]. Figure 4 shows the equilibrium melting point determination for P(HB-co-11%HV) and P(HB-co-11%HV) – 5% PEA blend, using the Hoffman-Weeks method. The equilibrium melting point for the crystalline phase in the blend, (164.3°C), is lower than the equilibrium melting point for the semicrystalline polymer in the pure state, (169.8°C).

Theses results indicate approximately some miscibility in the blend, until 30 wt% PEA.

Crystallinity of P(HB-co-11%HV) in the Blend

The crystallinities of the blends (Crb) and of the P(HB-co-11%HV) phase (CrPHA) can be calculated approximately from [8]

$$\mathrm{Crb} = (\Delta \mathrm{H\ f}/\Delta \mathrm{H\ f}^{\circ}) \times 100 \quad \text{and} \quad \mathrm{CrPHA} = \mathrm{Crb}/\mathrm{W}_{\mathrm{PHA}}$$

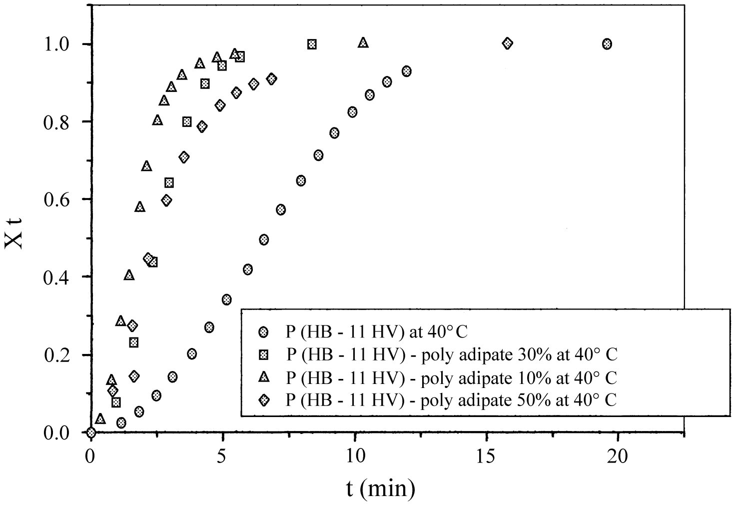

FIGURE 3 The crystallization behavior of the semicrystalline polymer, in P(HB-co-11%HV)/PEA blend samples of different composition, at 40°C. X_t is the relative fraction of crystallinity referred to the final amount of crystallinity developed in the same thermal condition at long time.

TABLE 3 Crystallization process study by DSC experimental data

ΔHf (J/g)	W_{PEA} (%)	Crb	W_{PHA}	$CrPHA$	ΔHc	$\Delta Hc/W_{PHA}$ (J/g)
60.87	0	41.52115	1	41.52115	38.3	38.3
60	5	40.92769	0.95	43.08178	46.46	48.90526
65.4	10	44.61119	0.9	49.56799	37.3	41.44444
78.8	30	53.75171	0.7	76.78815	40.4	57.71429
52.8	50	36.01637	0.5	72.03274	23.58	47.16

where $\Delta H\ f^{\circ}$ is the thermodynamics enthalpy of fusion per gram of copolymer and $\Delta H\ f$ is the experimental value obtained in the DSC experiment and W_{PHA} is the weight fraction. In this paper, $\Delta H\ f^{\circ}$ of PHB was used and the results have only qualitative value.

Table 3 shows these results. The crystallinities of the blends have smaller values than the crystallinities of the P(HB-co-11%HV) phase. The blend of 50 wt% has different behavior. The heats of blends crystallization (ΔHc) and $\Delta Hc/W_{PHA}$ are plotted *vs.* PEA content, in Figure 5. These values are dependent on the blend composition. The results indicate that the amorphous PEA component shows a remarkable effect on the copolymer crystallization. The P(HB-co-11%HV) – PEA blend have different behavior than PHB-Poly(lactide)(PLA) blend [8], and it may be explained by the miscibility of P(HB-co-11%HV) – PEA blend.

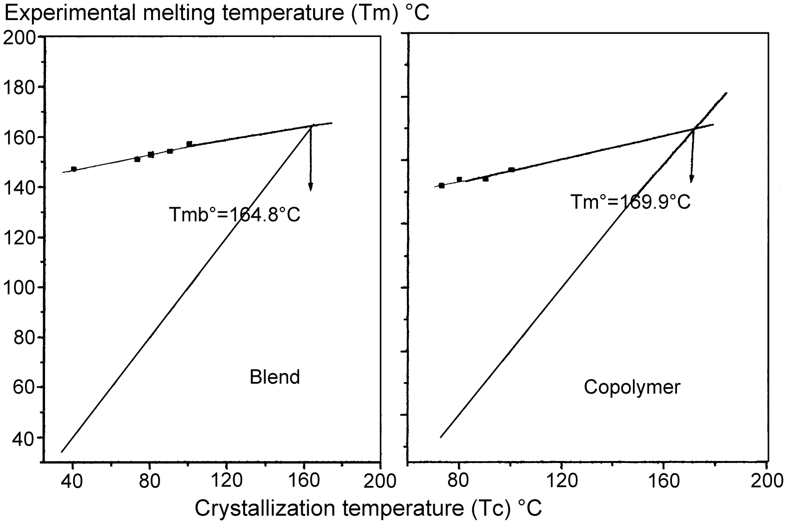

FIGURE 4 Hoffman-Weeks plots for copolymer and for the blend (wt% 5 of PEA). T_c: crystallization temperature and T_m: melting temperature after isothermal crystallization.

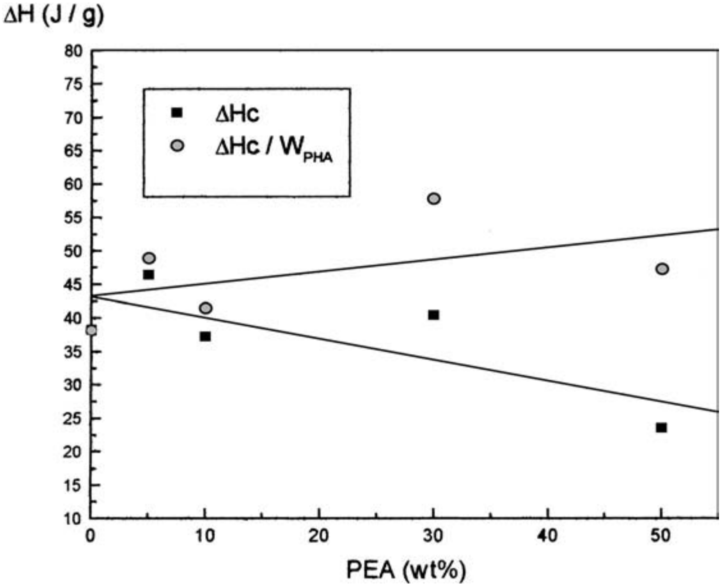

FIGURE 5 The heats of blends crystallization *vs*. PEA content.

Crystallization Kinetics

The DSC signal for isothermal thermograms of the blend presents a delay which represents an induction time. Table 4 shows induction times of P(HB-co-11%HV) – PEA blend of different compositions and different temperatures too. Induction time increases with increasing temperature for P(HB-co-11%HV) – 5% PEA blend and increases with increasing PEA concentration in the blend at 40°C but in all cases this value is lower than the corresponding to P(HB-co-11%HV). Then, the addition of PEA acts as nucleating agent. The induction time is a relevant parameter from processing and is associated with crystal nucleation. Nucleation is heterogeneous in nature and it is a thermally activated phenomenon that can be characterized by measuring the induction time as a function of the test temperature in isorhermal DSC. The induction time may be considered as the only detectable macroscopic parameter representative of the nucleation process.

The crystal growth is associated with the exothermic peak in DSC thermogram. The peak can be integrated to compute the mass fraction of crystallinity, X_t, assuming proportionality between the rate of crystallization and the heat flow measured by DSC.

$$X_t = \Delta H(t)/\Delta H_{total}$$

where X_t is the relative fraction of crystallinity referred to the final amount of crystallinity developed in the same thermal condition at long time [9]. As reported extensively in the literature macrokinetic models of isothermal crystallization are generally obtained by Avrami equation [7]:

$$X_t = 1 - \exp(-kt^n)$$

TABLE 4 Cold crystallization kinetics

Samples	*Temperature (°C)*	*Induction time (t_{ind}) (s)*
P(HB-co-11%HV)	40	45
P(HB-co-11%HV)-5%PEA	40	nd
P(HB-co-11%HV)-10%PEA	40	12
P(HB-co-11%HV)-30%PEA	40	24
P(HB-co-11%HV)	73	24
P(HB-co-11%HV)-5%PEA	73	12
P(HB-co-11%HV)	80	36
P(HB-co-11%HV)-5%PEA	80	12
P(HB-co-11%HV)	90	48
P(HB-co-11%HV)-5%PEA	90	18
P(HB-co-11%HV)	100	540
P(HB-co-11%HV)-5%PEA	100	42

The Avrami equation and the Avrami parameters are only a convenient means to represent empirical data of crystallization [10]. Plotting ln (-ln(1 − Xr)) *vs.* ln t and evaluating the slope, the Avrami exponent, n, and the intercept, the constant ln k [7]. The results of half-time, n and the Avrami constant value are shown in Table 5.

Some crystallization experiments on P(HB-co-11%HV) for the range of 37 − 50°C temperatures were carried out and the exponent n is close to 2.14. But the average value of Avrami exponent, n, for P(HB-co-11%HV) is 1.6 for the temperatures range of 73 − 100°C, it is close to the average value for P(HB-co-11%HV) – 5% PEA, (1.5). Additional information on nucleation, morphology and possibly even mechanism is necessary to fully interpret the exponent n [10].

The Avrami rate constant for copolymer is lower than the corresponding to the blend, because the crystallization rate of the blend is higher than that of the copolymer. The $1/t_{1/2}$ value can be considered as a crystallization rate measure. Figure 6 shows $1/t_{1/2}$ parameter *vs.* crystallization temperatures for the copolymer, the blend and the polyhydroxybutyrate (PHB) [11].

The P(HB-co-11%HV) – 5% PEA blend has the same behavior than PHB, which is the member of the polyhydroxyalkanoate (PHA) series with the highest nucleation rate. As a consequence, the PEA in a low content, acts as nucleating agent. This result is in agreement with the induction time analysis.

Mechanical Properties of the Blends

The mechanical properties of the blend were obtained. Tensile properties of the blends are shown in Table 6. The increase in polyadipate content produces a decreasing of the modulus and the stress at break. Also the

TABLE 5 Avrami parameters

Temperature (°C)	*n(I)*	*n(II)*	*− ln k(I)*	*− ln k(II)*	$t_{1/2}(I)$ *(min)*	$t_{1/2}(II)$*(min)*
37	2.13	–	13.2	–	7.23	–
40	2.14	–	13.06	–	6.57	–
43	2.08	–	12.68	–	6.20	–
46	2.08	–	12.5	–	5.69	–
50	2.12	–	12.3	–	4.52	–
73	1.56	1.61	8.78	7.54	3.19	1.4
80	1.77	1.25	9.78	5.72	3.28	1.11
90	1.7	1.31	10.12	6.59	5	1.87
100	1.44	1.68	10.71	9.33	9.21	3.49

I: P(HB-co-11%HV).
II: P(HB-co-11%HV)-5%PEA.

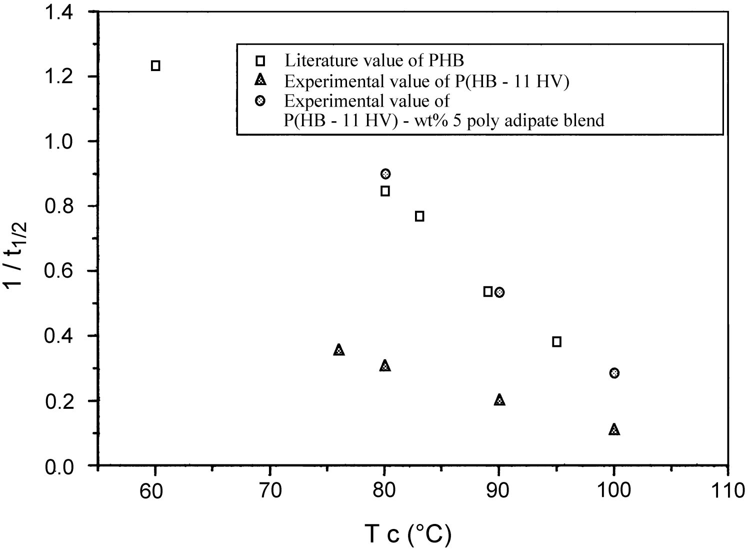

FIGURE 6 Comparison of the crystallization rates for the copolymer and the blend (wt% 5 of PEA).

TABLE 6 Mechanical properties

Samples	*Modulus (MPa)*	*% Elongation*	*Stress at break*
P(HB-11%HV)	8.62	14	19.69
P(HB-11%HV)-wt% 10 polyadipate	4.94	11	7.72
P(HB-11%HV)-wt% 30 polyadipate	4.26	8	6.42
P(HB-11%HV)-wt% 50 polyadipate	0.93	6	0.79

elongation decreases with the increasing of PEA content. This effect may be explained by the increased blend crystallinity.

Thermal Decomposition

Thermal decomposition of the blends was studied by means of thermogravimetry. Table 7 shows two temperatures: T_{onset} (it indicates the beginning of the thermal decomposition) and T_{max} (it indicates the midpoint temperature at which the rate of thermal decomposition is highest). T_{onset} is the same in the blend and in the polymers but T_{max} decreases in the blend. Table 7 shows the apparent activation energy. Theses values were calculated using the following expression:

$$-d\alpha/dt = ko\ \exp(-Ea/RT)(1-\alpha)$$

TABLE 7 Thermal decomposition

Samples	T_{onset} (°*C*)	T_{max} (°*C*)	*Ea* (*kJ*/*mol*)	*Lineal correlation* (*r*)	α
P(HB-co-HV)	229	280	311	0.99915	0.03–0.87
P(HB-co-HV)–wt% 50 polyadipate	229	275.5	258	0.99418	0.022–0.81
Polyadipate	229	355/408	71.5	0.99412	0.01–0.83

and they are in agreement with reported value in others papers [12, 13], where α is the degree of volatilization (weight loss fraction). There is an influence between the two compound in the blend, because the PEA activation energy increases and the P(HB-co-HV) activation energy decreases in comparison with the pure compounds.

CONCLUSION

The PEA addition ($<$ wt% 30) to P(HB-co-11%HV) is in favor of the quick crystallization of the copolymer. It forms a miscible blend and the elastic modulus decreases. Avrami equation was applied and the exponent was determined close to 2. Thermal decomposition shows that the PEA addition decreases the activation energy of the process.

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