

Effects of hydroxyvalerate contents in thermal degradation kinetic of cellulose acetate propionate/poly(3-hydroxyalkanoates) blends

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Received: 30 April 2011 / Accepted: 12 December 2011 / Published online: 7 January 2012
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Abstract Thermal stability of polymers is an important parameter that determines the application as well as the processing conditions. The green polymers have shown low thermal stability, such as the polyhydroxyalkanoates (PHAs). The PHAs with different comonomers containing hydroxyvalerate (HV) were studied. It was seen that the green polymer showed a fast thermal degradation process. The addition of the HV comonomer modified this profile and the thermal degradation kinetic. The blend prepared between the PHAs and other polymers can modify the thermal degradation process of the green polymers. In the present study, blends of cellulose acetate propionate and PHAs were prepared, and the thermal degradation kinetics of these blends were evaluated. It was observed that the cellulose acetate propionate (CAP) phase in the blends modified the thermal degradation process and kinetic profile of the PHA phase. In the blends, the thermal stability of the PHAs was slightly modified because of CAP reducing the reactivity of the PHAs. On the other hand, the thermal stability of the CAP phase in the blends is not largely modified by the PHA phase. However, the hydroxyvalerate comonomer decreases the reactivity of the CAP phase at the start of thermal degradation of the same. The interaction between the phases promotes the synergetic interaction, which slightly improves the thermal stability of the two polymers blends.

Keywords Thermal degradation kinetic · PHB · P(HB–HV) · CAP · Blends

Introduction

The green polymers have occupied an important place in the sustainable development, mostly by environmental concern [1]. Among these polymers, it is possible to highlight cellulose polysaccharide as one of the most important biomass resources, and polyhydroxyalkanoates (PHAs) from bacterial biosynthesis [2]. Some of the disadvantages of the green polymers are their unsatisfactory mechanical properties and thermal behavior in thermal processing. In principle, the unsatisfactory properties of the green polymers can be significantly modified when blended with others polymers [1–5]. PHAs with short side chains are associated with higher crystallite, narrow processing windows, and a relatively higher production cost, which have limited the use of these polymers [1, 6, 7]. The cellulose is a polymer with the highest crystalline nature and is insoluble in common solvents. To modify of these properties, derivatives of the cellulose are obtained between the substitutions of the hydroxyl groups for the ester groups. However, the cellulose esters are stiff due to a high glass transition temperature (T_g); this behavior can be modified by a blend of cellulose esters with other natural polymers [8–11].

Some specific blends of cellulose derivatives with PHAs were studied by Scandola [12] and Buchanan [9, 13]. Scandola noted that the PHB forms miscible blends with the cellulose esters [12]. On the other hand, Buchanan studied the blends of cellulose esters with the poly(3-hydroxybutyrate–hydroxyvalerate) [P(HB–HV)] copolymers and reported that the copolymers also formed miscible blends, limited by the HV content [9, 13]. This blend of cellulose derivatives with PHAs can offer opportunities for lowering the cost and enlarging the range of applicability of these biopolymers [5, 9, 13].

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Although a number of studies have been reported on the miscibility, and thermal and thermal–mechanical behaviors of the cellulose derivatives/PHAs blends, the thermal degradation behavior of these blends has been little studied [4, 8, 9, 12, 13]. The thermal degradation process of the polymer blends is influenced by the degradation conditions, structure of the components of the polymer blend, and by the potential co-reactivity between the components and/or their degradation products [5]. It is important to understand that the thermal degradation process in potential commercial materials to control, accelerate, or retard this process [5, 14].

There is a great deal of information in the literature about the thermal degradation mechanism of PHB, which occurs by random chain scission on the ester group [3]. Kunioka and Doi studied the thermal degradation on the isothermal conditions of the PHB and copolymers with different HV contents, observing the rate of random chain scission at the ester groups. Studies regarding the thermal degradation of cellulose derivatives are little explored in the literature [3]. Gongwer [15] studied the thermal degradation of the cellulose acetate butyrate observing a great variety of competitive and parallel reactions involving the main chain as much as the functional groups. The aim of the present study was to assess the effect of PHAs with different HV contents produced on the thermal degradation kinetic behavior of cellulose/PHAs blends, by means of the thermogravimetric analysis (TGA) data.

Experimental

Materials

Cellulose acetate propionate (CAP) was purchased from Aldrich (M_m 15,000 Da) with acetate 0.6% and propionate 42.5% as mass contents. The bacterial polyesters used were poly(3-hydroxybutyrate—PHB) supplied by PHB Industry S/A, Brazil (M_m 640,000 Da), and the copolymers of P(HB–HV) with 8% mol (M_m 92,000 Da), 14% mol (M_m 153,000 Da), and 22% mol (M_m 188,000 Da) of HV comonomer were purchased from Aldrich.

Preparation of blends

Thin films of the CAP/PHAs blends with mass ratios of 100/0, 95/5, 90/10, and 0/100 were prepared by casting; the polymers were solubilized in chloroform from 3% m/v . The solution of the blend was stirred for 12 h and allowed to remain at rest for 6 h. Next, the solution was poured in a Petri dish for the solvent to evaporate at 30 °C for 24 h, and then kept at 40 °C under vacuum for 12 h.

Thermal degradation and kinetic analysis

The study of thermal degradation of the films was carried out using Thermobalance TA Instruments–SDT 2960, in helium atmosphere (100 mL min⁻¹). The profiles of the mass losses were obtained in the temperature range of 25–900 °C at heating rates of 5, 10, 15, and 20 °C min⁻¹ in a platinum pan with a sample of about 10 mg for each analysis.

Kinetic analysis

Trustworthy conclusions about the thermal degradation kinetic behavior of the polymer materials can be obtained by the identification of the kinetic model, often referred to as the reaction model, together with the Arrhenius parameters, such as pre-exponential (A) term and activation energy (E_a). In the kinetic analysis of polymers, it is convenient to express the variation of the amount of mass in terms of the reaction extent (α) defined by Eq. 1 [14, 16, 17].

$$\alpha = \frac{m_i - m}{m_i - m_f}, \quad (1)$$

where m is the mass of the sample at a certain time, and m_i and m_f are the initial and final mass values, respectively, of the reaction range analyzed. The reaction rate for the non-isothermal degradation conditions is given by Eq. 2:

$$\frac{d\alpha}{dT} = \frac{A \exp\left(-\frac{E_a}{RT}\right) f(\alpha)}{\beta}, \quad (2)$$

where $d\alpha/dT$ is the reaction rate, A is the pre-exponential factor of Arrhenius, $f(\alpha)$ is the reaction model, E_a is the activation energy to given reaction extent, T is the absolute temperature, β is the heating rate, and R is the ideal gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The reaction model for a solid-state reaction depends on the reaction mechanisms in the literature, which have been presented as a rigorous discussion on the function assumed by the reaction model [14, 17–20]. One of the few difficulties encountered in using Eq. 2 is the determination of the E_a of a reaction without having any previous knowledge about the reaction model. There are several methodologies to evaluate the thermal degradation kinetics in this case. These methods are based on the assumption that the reaction mechanism is independent of the heating program, using multiple heating rates. These methods, such as Friedman and Ozawa–Wall–Flynn (O–W–F), are known as isoconversional [18–20].

The O–W–F method involves measuring the temperatures corresponding to the fixed values of α from the experiments at different heating rates, and plotting $\ln(\beta)$ against $1/T$ in agreement with the Eq. 3.

$$\ln(\beta) = \ln \left[A \frac{f(\alpha)}{d\alpha/dT} \right] - \frac{E_a}{RT}. \quad (3)$$

The slope of the plot from the left-hand side of the Eq. 3 and $1/T$ for a given reaction extent is $-E_a/R$ and provides the activation energy for one [18–20].

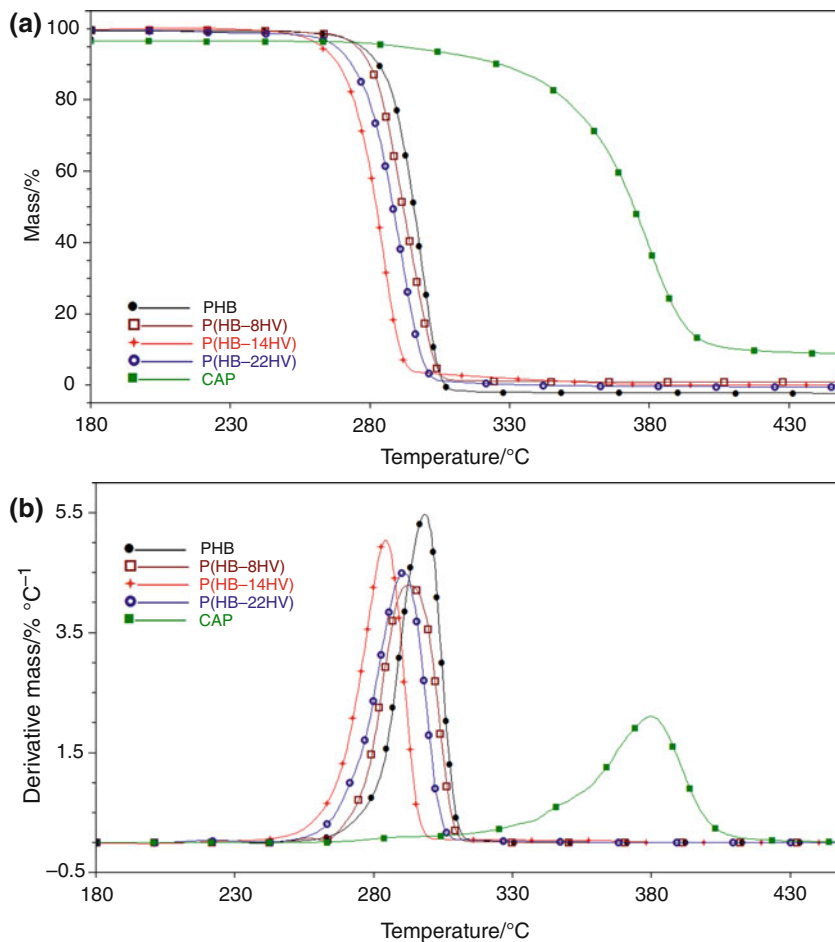
The Friedman method is based on Eq. 4. By plotting $\ln[(d\alpha/dT)\beta]$ against $1/T$ for a given reaction extent, the slope is $-E_a/R$, which supplies the activation energy to this reaction extent [21]

$$\ln\left(\frac{d\alpha}{dT}\beta\right) = \ln[Af(\alpha)] - \frac{E_a}{RT}. \quad (4)$$

It has been observed that E_a is not the same for all the reaction extents in the thermal degradation process of complex materials. If E_a varies on α , then the results should be interpreted in terms of the process which involves several steps that have different activation energies [18–20]. A limitation of both the Friedman and O–W–F methods is the determination of the reaction model. The use of the Coats and Redfern (CR) method given by Eq. 5 has been suggested in the literature combined with the Friedman and O–W–F methods to determine the reaction model [16, 20, 22]

$$\ln\left(\beta\frac{g(\alpha)}{T^2}\right) = \ln\left[\frac{AR}{E_a}\right] - \frac{E_a}{RT}. \quad (5)$$

Fig. 1 **a** Mass curves profile and **b** derivative mass curves for CAP, PHB, and copolymers with different HV contents at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$, in helium atmosphere



The left-hand side of the Eq. 5 is plotted against $1/T$ (absolute temperature) for each heating rate. The integral form of the reaction model is used for the given reaction extent and temperature. The curves are plotted for all the reaction models, and the characteristic reaction model for the process of thermal degradation analyzed is the one that presents the correlation coefficient closest to the unit [16, 20, 22].

These methods permit assessing the interdependence between the activation energy and mass conversion fraction, and obtain reaction model, as well as the influence of the components of the blend on the thermal degradation process [18–20].

Results and discussion

Thermal degradation non-isothermal study of PHAs and CAP

Thermal degradations of CAP and PHAs were studied by the non-isothermal conditions, and their mass losses at different heating rates were evaluated. The shapes of the PHAs and CAP mass curves (Fig. 1) do not change with

the variations of the heating rate. The thermal events are only slightly dislocated to higher temperature values with higher heating rates. This phenomenon is characteristic of the equipment, which detects the events in higher temperatures with higher heating rates, although they have begun in the characteristic temperature [23].

The thermal degradation process of the PHAs takes place as a single step of mass loss and occurs in a short interval of temperature, between 240 and 310 °C. The mass curve profile of CAP exhibits two steps of thermal degradation. The first step is at maximum degradation temperature around 379 °C. This step could be associated with breaking the bone associated to functional groups and weak groups in the chain [15, 23], while the second degradation step of CAP is not observed with a maximum peak in the DTG curve. In general, this step can be associated with thermal degradation of the carbon structure. The maximum degradation temperature peak for CAP occurs between 349 and 380 °C at heating rates of 5 and 20 °C min⁻¹. The derivative thermogravimetric curve for CAP does not show symmetry, as observed for PHAs, between the beginning and the end of the step of thermal degradation. This suggests that in the beginning stage of thermal degradation, events can be put upon, which were not resolved through the analysis of TGA. The mass loss observed below 150 °C for CAP can be ascribed to the evaporation of water present in the sample.

It is evident that CAP is thermally more stable than PHAs because the thermal degradation of the PHAs starts earlier and occurs in narrower temperature intervals. Similarly, the mass loss profile is dislocated to higher temperatures at higher heating rates; the maximum degradation temperature (T_{\max}) is also one. The T_{\max} of copolymers with hydroxyvalerate is slightly lower with pure PHB and is modified by the addition and increment of the hydroxyvalerate content. The T_{\max} of the copolymer with 22% HV content is relatively close to PHB (Fig. 2b). The sequence distributions of the hydroxyvalerate units in copolymers have been found to be random. In general, the physical properties of copolymers strongly depend on their comonomer composition as well as their distribution sequence [24, 25]. For bacterial copolymers, the thermal degradation behavior is dependent on the substituent type in the side chain and stereoregularity of the macromolecule. The HV unit has ethyl groups in the side chain instead of the methyl group of the HB unit, which promote a change in the stereoregularity and chemical characteristics of the copolymers [24–27]. It was observed that the addition of the HV unit reduces the thermal degradation behavior up to 14% moles of the HV content (Fig. 1). For 22% moles of the HV content, the thermal degradation behavior is intermediary to the other copolymers studied.

The secondary carbon atoms in the chain can suffer scission in the hydrogen carbon leakage with lower energy

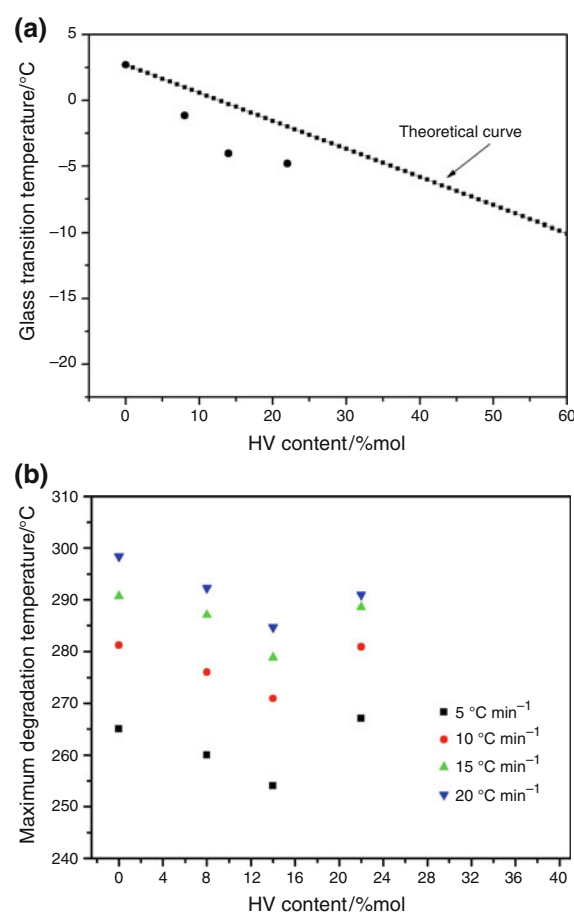
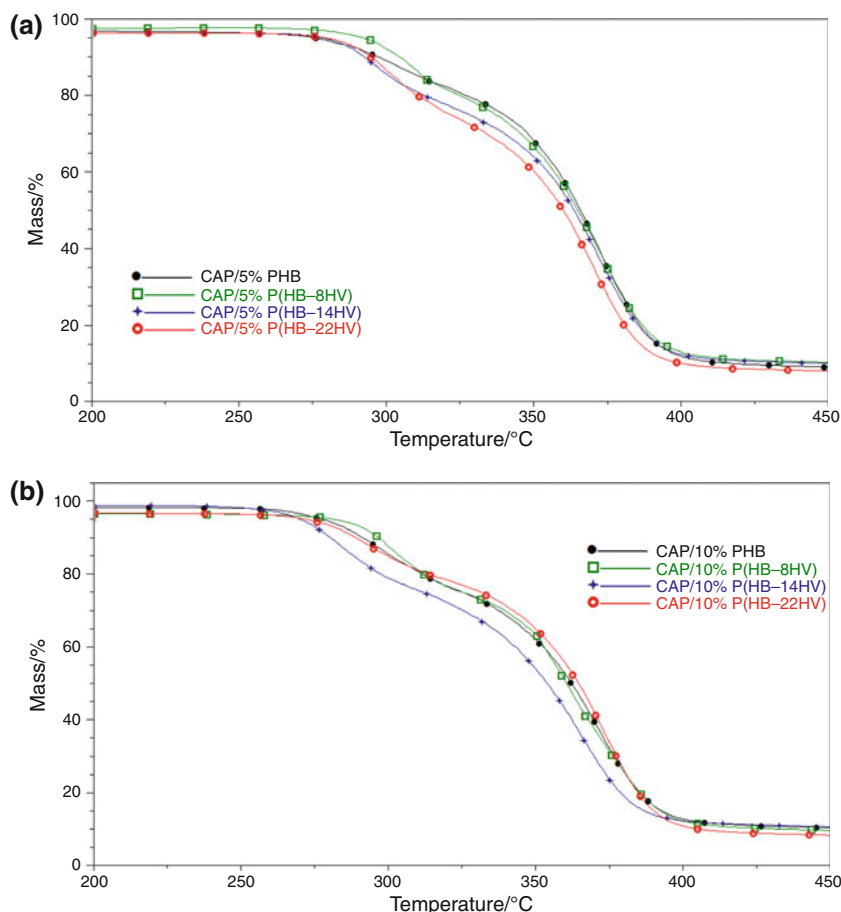


Fig. 2 **a** Glass transition temperature determined by DSC [26] and theoretical T_g determined by the mixture simple rule ($T_g = m_1T_{g1} + m_2T_{g2}$) [25, 26] against HV content; **b** maximum degradation temperature at different heating rates against HV content

than the primary carbon atoms [7, 28]. The break of links as C–H in the secondary carbon atoms would lead to the formation of the free radicals, which in the case of the copolymers should increase with the addition of the HV content by the presence of the secondary carbon atoms. In this way, the thermal stability of the copolymers could be decreasing in comparison with the homopolymer PHB [7, 28]. However, the above mentioned behavior is not observed because, with 22% of the copolymer, the thermal stability is improved in comparison with the content of 14%, whereby this can be noted independent of the heating rate. The above mentioned behavior would be related to the random distribution of the HV unit and the anomalous distribution of this comonomer. The presence of the HVHV and HV units in the anomalous random distribution of this comonomer has been observed in the literature, which takes into account the anomalous behavior in the thermal and mechanical properties of the different compositions of the HV units in the copolymers [25, 26, 29].

Fig. 3 Mass loss curves for blends of CAP with **a** 5% and **b** 10% of P(HB–HV) with different HV contents, in helium atmosphere at $20\text{ }^{\circ}\text{C min}^{-1}$



The anomalous behavior as a function of the comonomer's content was also observed for the T_g of the copolymers studied (Fig. 2a). The present findings of the study compare well with those presented by the research group in the literature [26]. Similar to the behavior of T_g , the T_{max} also almost decreases lineally (Fig. 2b) with the addition of up to 14% mol of the HV content. When 22% mole of hydroxyvalerate content is present in the copolymer, a modification in the tendency for the characteristic temperature to be decreasing is observed. Although the values of T_g are acceptable because of the presence of the HV content, it occupies a larger free volume to reduce the value of T_g . For the thermal stability behavior, this is in contrast to what was mentioned previously regarding the increase of the secondary carbon atoms in the monomer unit. The anomalous random distribution of the HV units influences the thermal stability of the copolymers with hydroxyvalerate, particularly in case of the 22% mole content studied.

Thermal degradation non-isothermal study of blends

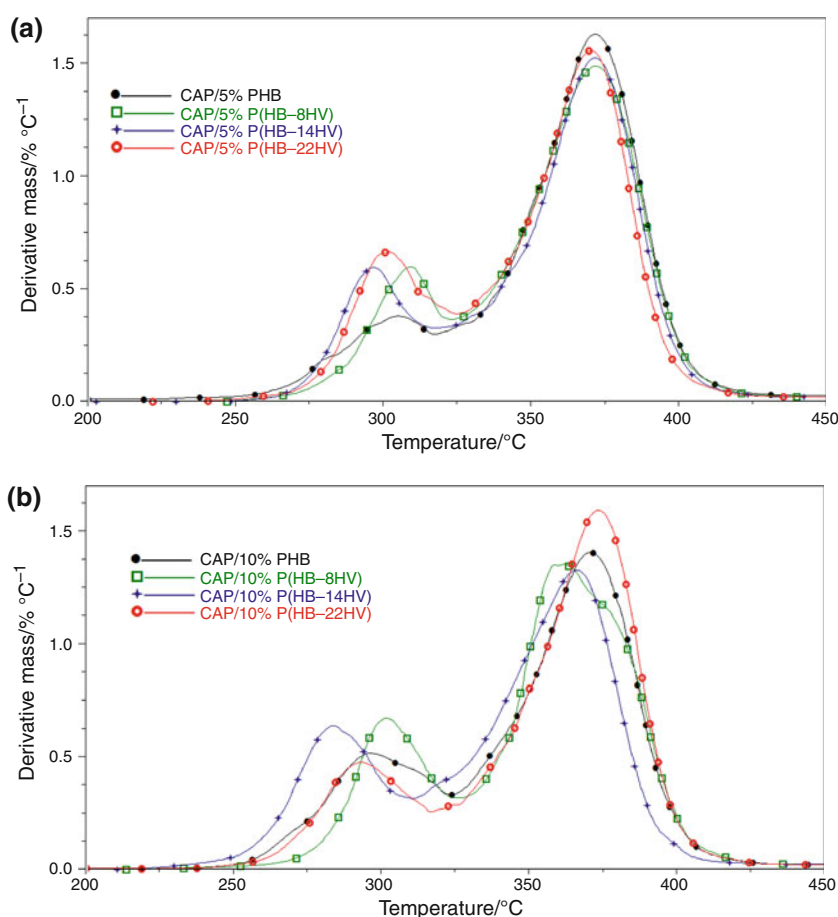
The mass loss profiles for the CAP/PHAs blends with 5 and 10% of the P(HB–HV) demonstrated three separate

degradation steps (Fig. 3). The first step of thermal degradation for the blends could be assigned to the thermal degradation of the PHAs content in the blends, while the other steps could be assigned to the CAP.

It is important to note that the derivative curves of mass loss for the blends are partially overlapped (Fig. 4). This could be due to the end of the thermal degradation process of PHAs coinciding with start of the thermal degradation process of CAP. In the blends, the mass loss for the first step of thermal degradation is slightly dislocated to higher temperature in comparison to the mass loss of PHAs individually. In the CAP/PHAs blends, it was observed that the addition of the hydroxyvalerate content modified the profile of thermal degradation in the PHA phase in the blends (Fig. 4).

The DTG is a temporal rate of mass loss commonly used to detect the subtle effects, which cannot be observed by only the mass loss curve. The inflection points in the mass curve as well as the shape of the curve are associated with the completion of the steps in a series of reactions, or the changes in the mechanisms during a reaction [23]. The shape of the DTG curves for the blends of CAP and PHAs are modified with the addition of the hydroxyvalerate content. The shape of the DTG curve for the PHB blends is

Fig. 4 Derivative mass curves at $20\text{ }^{\circ}\text{C min}^{-1}$ for blends of CAP with **a** 5% and **b** 10% of P(HB–HV)



not defined in comparison with the blends with the HV content, whereby the shape is more defined, and the T_{\max} values are slightly dislocated to higher temperatures.

Although the T_{\max} dislocates slightly to higher value (Fig. 5), its behavior in relation to the HV content observed in the thermal degradation of the copolymers is not modified. The thermal degradation behavior of CAP has a slight decrease in the T_{\max} values in the blends with PHAs as well, as observed by the mass curve. The increase of the HV content did not modify this behavior. In a mixture, the interaction among the components can originate interactions among the free radicals formed that may or may not be harmful for either or both of the components [30]. In addition to an influence of the hydroxyvalerate content, it was also observed that the amount of PHAs taking place changed in the T_{\max} of the mixture (Fig. 6). For the blends with 10% in mass, the behavior of the thermal degradation suffers an increment in the characteristic temperatures for the larger temperatures as a function of the addition of the HV content. This was not observed for the blends with 5% of PHAs (Fig. 6).

The addition of PHAs in the blends promotes an increase of the T_{\max} at the first step in comparison to the T_{\max} of the PHAs not blended (Fig. 2). For blends with 5%

of PHAs, the increase in the T_{\max} is more significant in comparison with the blends with 10% of PHAs. Although the T_{\max} has been decreasing with the addition of the HV content, it is bigger in comparison to the T_{\max} of the mixture with PHB. On the other hand, the T_{\max} of the second step is lower in comparison with the CAP individual. The addition of PHAs in the blends modified the profile of thermal degradation of these polymers. Such an observation could indicate that the presence of CAP in the blends slightly improves the thermal stability of the PHA phase.

Kinetic analysis of the PHAs, CAP, and blends

The kinetic parameters were obtained from the non-isothermal thermogravimetry data. The E_a associated with the thermal degradation processes of the P(HB–HV), CAP, and P(HB–HV)/CAP blends on the fraction of mass conversion was determined using the Friedman and O–W–F methods, as described in the “Experimental” section. The assessment of E_a was made in a range of the fraction of mass conversion of $5 \leq \alpha \leq 90\%$. The activation energy of the PHAs is dependent on α (Table 1). For the fraction of mass conversion investigated, the average of the E_a was

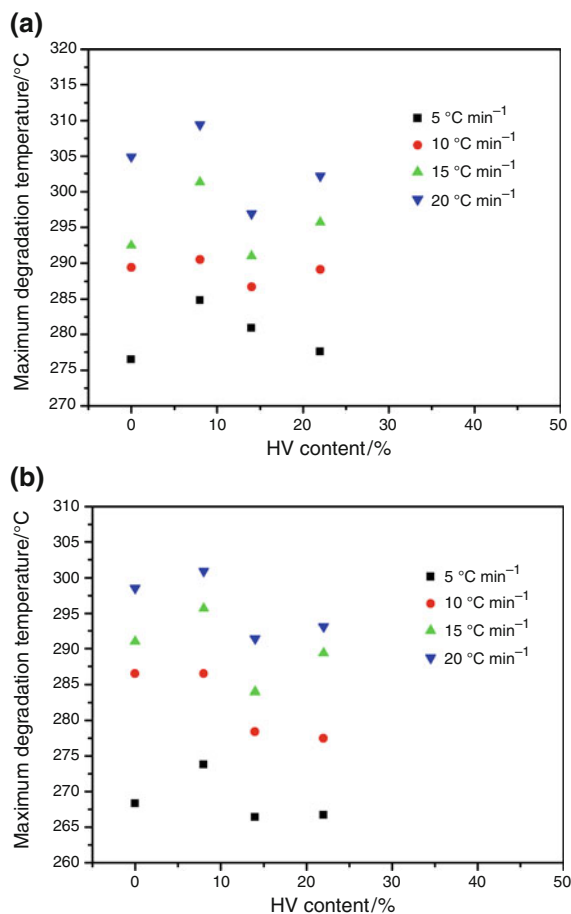


Fig. 5 Maximum degradation temperature behavior to first step against HV content at different heating rates for blends of CAP with **a** 5% and **b** 10% of P(HB-HV)

$95 \pm 10 \text{ kJ mol}^{-1}$ for PHB, $90 \pm 10 \text{ kJ mol}^{-1}$ for P(HB-8HV), $104 \pm 7 \text{ kJ mol}^{-1}$ for P(HB-14HV), and $120 \pm 13 \text{ kJ mol}^{-1}$ for P(HB-22HV). The activation energy for thermal degradation process of CAP changed drastically with the fraction of mass conversion, whereby the average E_a obtained was $163 \pm 21 \text{ kJ mol}^{-1}$. While the activation energy of the PHAs decreases slightly with the fraction of mass conversion, the one of CAP increases. The variation in the activation energy of CAP could be attributed to the linkage scissions in the functional groups followed by the scissions of linkage on the chain, which bonds the different activation energies and mechanisms of thermal degradation [15].

Thermal degradation involves reactions of the solid-state type, which, given the origin of the solid and volatile materials and the difference of the other degradation processes, occurs in the bulk of the polymers [31]. Such reactions take place by one of the several elementary mechanisms, as well as the combinations of these mechanisms. In general, the dependence of E_a on the fraction of mass conversion is associated with the occurrence of

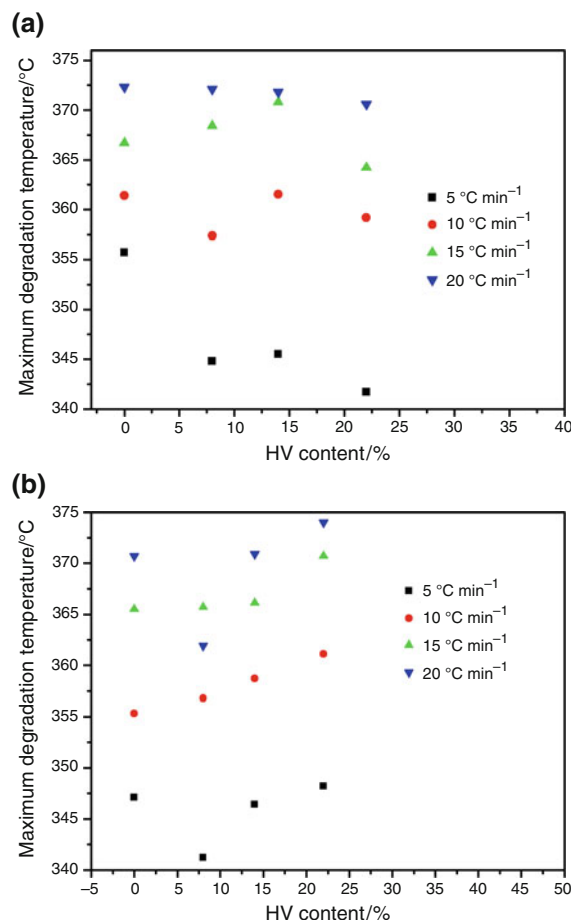


Fig. 6 Maximum degradation temperature behavior to second step against HV content at different heating rates for blends of CAP with **a** 5% and **b** 10% of P(HB-HV)

parallel, consecutive, and irreversible reactions on the thermal degradation process of the polymers [32]. In some cases, the thermal degradation of the polymer materials is not associated with the dependence of E_a on α . This particular case was observed for poly(propylene succinate), a biodegradable aliphatic polyester [32]. It was observed by those authors that the dependence of E_a on the fraction of mass conversion values has two separate regions: up to 10% in which E_a increases, and above 10% the average value of E_a does not significantly change. The obtained results show that the thermal degradation processes occur through the cleavage of linkage with similar energies to mass conversion above 10% [32].

In case of the PHAs thermal degradation process, the kinetics showed dependence of E_a on α , thereby indicating that the degradation process took place by the complex reactions with participation of the different mechanisms associated with the different levels of activation energies and linkage bond energies [32–34]. Fraga [8] obtained the activation energies by applying the isoconversional Friedman method for P(HB-8%HV), whereby the average

Table 1 Relationship of activation energy on $5 \leq \alpha \leq 90\%$ for thermal degradation of CAP and P(HB-HV) by Friedman and O–W–F methods

$\alpha/\%$	Activation energy by Friedman method				Activation energy by O–W–F method					
	P(HB–HV)		CAP		P(HB–HV)		CAP			
	HV content/% mol				HV content/% mol					
	0	8	14	22	0	8	14	22		
5	84	91	100	132	133	91	84	95	133	142
10	88	101	102	129	137	93	88	99	135	149
15	103	101	109	132	143	94	90	101	137	150
20	104	100	110	132	146	96	92	103	138	151
25	105	99	111	131	148	97	93	104	138	153
30	105	98	111	130	150	97	93	105	139	154
35	105	97	111	129	152	98	94	106	138	155
40	104	96	111	128	155	99	94	107	139	156
45	103	95	110	126	157	99	95	108	139	158
50	102	93	109	125	160	100	95	108	139	159
55	100	91	108	123	163	100	95	109	139	160
60	98	89	106	120	167	100	95	109	138	162
65	95	87	104	117	171	101	95	109	138	164
70	92	84	102	114	176	101	95	109	138	166
75	88	80	99	110	182	101	95	109	137	169
80	84	76	96	104	189	100	95	109	136	172
85	79	70	92	98	198	100	94	109	135	176
90	72	63	87	89	210	93	94	108	133	181

apparent activation energy determined for the mass conversion ranging from 10 to 90% was $111 \pm 8 \text{ kJ mol}^{-1}$. According to Fraga [8], considerable variations among the reported E_a values may be found when analyzing the literature: 74 kJ mol^{-1} for PHB determined by Osawa's method; 300 and 370 kJ mol^{-1} for PHB and P(HB–30%HV) respectively, as determined by the CR method; and 311 kJ mol^{-1} for P(HB–11%HV). These variations in intensity on E_a could be associated with parameters, such as molar mass, sequence of distribution of the comonomers, and the fact whether the kinetic method applied was isoconversional or not.

By comparing the results obtained with the application of the Friedman and O–W–F methods for the determination of the activation energy, it is possible to observe that the values of Friedman method are slightly higher than the values determined by O–W–F method. However, both methods reveal the same trend on E_a as regards the range of the α evaluated. For PHB, lower values of E_a were observed in comparison to the copolymers with hydroxyvalerate, except for P(HB–8HV), which showed lower values of the activation energy. The CAP activation energy also showed a similar tendency on the fraction of mass conversion with regard to both the methods.

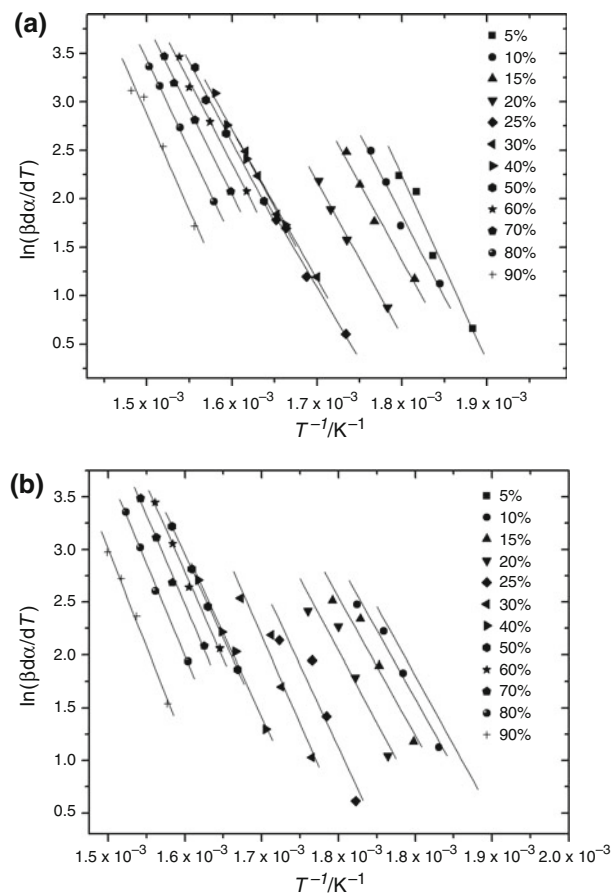


Fig. 7 Isoconversional Friedman plots ($5 \leq \alpha \leq 90\%$) of **a** CAP/5% P(HB–14HV) and **b** CAP/10% P(HB–22HV) blends

Isoconversional plots for the CAP/PHAs blends are shown in Fig. 7 for the Friedman method, and in Fig. 8 for the O–W–F method. Two different regions in the isoconversional curves are observed. These regions correspond to each step of the thermal degradation process seen in the TGA curves of the blends. The irregularity between the isoconversional curves is more pronounced in the blends and more marked in the overlapped region. The irregularity in the spacing of the isoconversional curves (Figs. 7 and 8) is related with the break of leakage with the different levels of energy occurring at the same time in both the components of the blend, as well as the several steps and different mechanisms of the thermal degradation [18–20]. It is possible to observe through the isoconversional curves that the overall thermal degradation process of the blends had shown a complex thermal decomposition with the reactions which involved different mechanisms.

The start of the thermal degradation process in the blends showed levels of activation energy which were very different (Figs. 9 and 10) in comparison to those observed in the PHAs (Table 1). A strong variation in E_a on the α results of the process, which involves a series of parallels, consecutive, and irreversible reactions that occur with the polymers,

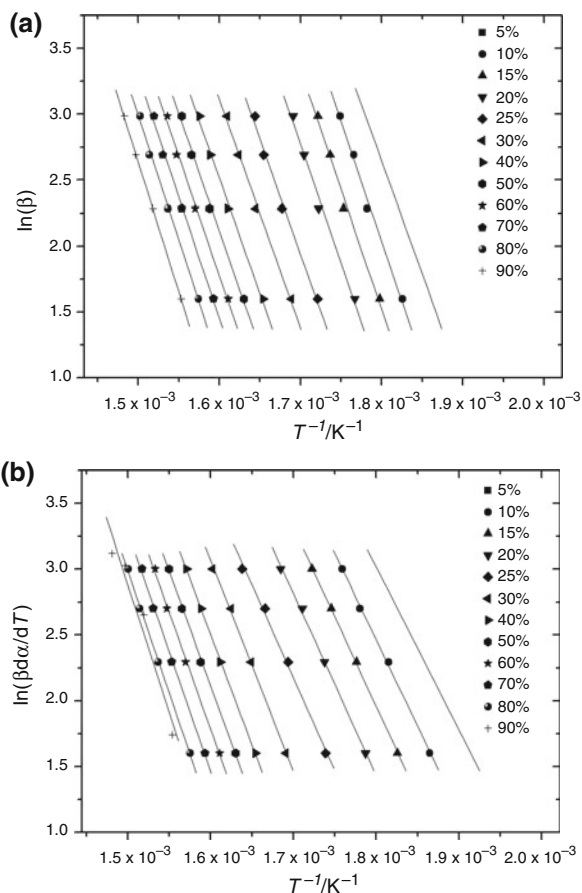


Fig. 8 Isoconversional Ozawa–Wall–Flynn plots ($5 \leq \alpha \leq 90\%$) of **a** CAP/5% P(HB-14HV) and **b** CAP/10% P(HB-22HV) blends

shows the complexity of these reactions, which accentuates the fractions of mass conversion to be lower than 30% [8, 18, 34]. This range did not show a tendency of compartment between the blends or the composition of the components, possibly because the end and the beginning of the processes of thermal degradation of the each component of the blends happen in this range. After the beginning step of the free radical formation, the thermal degradation can form cyclic compounds or inter- or intramolecular reactions, impeding the thermal degradation process or accelerating it [5, 31, 34]. In the blends, both polymeric ones can suffer scissions of their linkage, and reactions among them can happen. This could justify the reason for the behavior of the activation energy level at the beginning of the process of thermal degradation of the blends.

Similar to individual polymers, the determination of the activation energy from the Friedman and O–W–F methods showed similar differences in the intensity of E_a . However, the compartment on the fraction of mass conversion is comparable between the two methods. In agreement to Maciejewski [19], the kinetic description of the solid state reactions is influenced not only by the complicated nature of the process but also by the method of calculation.

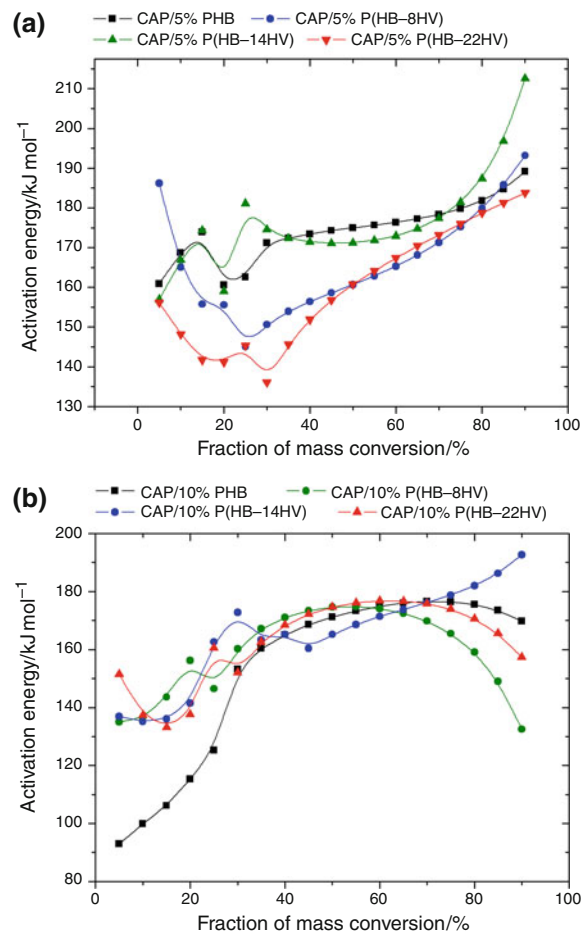


Fig. 9 Activation energy versus α plot ($5 \leq \alpha \leq 90\%$) to **a** CAP/5% P(HB-HV) and **b** CAP/10% P(HB-HV) by Friedman method

The CR method was used to determine the reaction model [16–18]. By this method the thermal degradation of the PHAs shows a reaction model of the type sigmoidal. For PHB and P(HB-8HV), among all the models, sigmoid is best adjusted not only for the coefficient of linear correlation, but also for the values of activation energy in comparison to the medium values obtained by the Friedman and O–W–F methods. For PHB and P(HB-8HV) the reaction model was A3 ($f(\alpha) = 3(1 - \alpha)[- \ln(1 - \alpha)]^{-1/2}$). Santos [35] evaluated the thermal degradation kinetic of the PHB, the authors obtained that initial thermal degradation of the PHB is governed by a sigmoidal model. For the copolymers with 14 and 22% of hydroxyvalerate the reaction model was A4 ($f(\alpha) = 4(1 - \alpha)[- \ln(1 - \alpha)]^{-1/3}$). This explains the reason for a little variation of the activation energy found for PHAs; because there is formation of several reactive points simultaneously that grow along of the process during the thermal degradation, which is in agreement with the sigmoid models [16–18, 22]. This implicates in the formation of several degradation microstates, which at the same time are degrading the macromolecules of the PHAs breaking leakage with similar levels

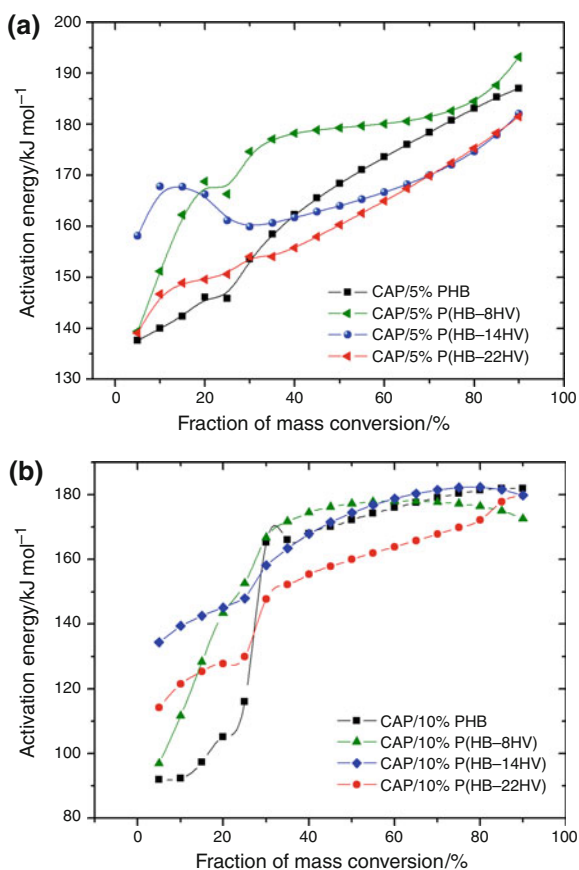


Fig. 10 Activation energy versus α plot ($5 \leq \alpha \leq 90\%$) to **a** CAP/5% P(HB–HV) and **b** CAP/10% P(HB–HV) by Ozawa–Wall–Flynn method

of energy resulting in a fast thermal degradation of the material, as shown by the thermogravimetric curves (Fig. 1a).

The CAP's medium activation energy values of $163 \pm 21 \text{ kJ mol}^{-1}$ by the method of Friedman, and that of $160 \pm 21 \text{ kJ mol}^{-1}$ by the method of O–W–F were obtained. The CR method showed a better coefficient of lineal correlation, for reaction model which was the diffusion mechanism D1 ($f(\alpha) = 1/2\alpha$) [16–18, 22]. In agreement with this reaction model, there is a formation of nuclei that is diffused by the polymer during thermal degradation. With the formation of a single microstate and consequently the growth of this, the larger levels of energy are necessary to break the leakage with different levels of energy.

For the blends of CAP with 5 and 10% of PHAs, the reaction model that showed better coefficient of lineal correlation was the diffusion mechanism. However, different from the CAP, the blends were degraded in agreement with the diffusion model D3 ($f(\alpha) = 3/2(1 - \alpha)^{2/3} [1 - (1 - \alpha)^{1/3}]^{-1}$) [16–18, 22]. The change of the reaction model for the blends is probably due to the addition of the PHAs content, where the polymeric–polymeric

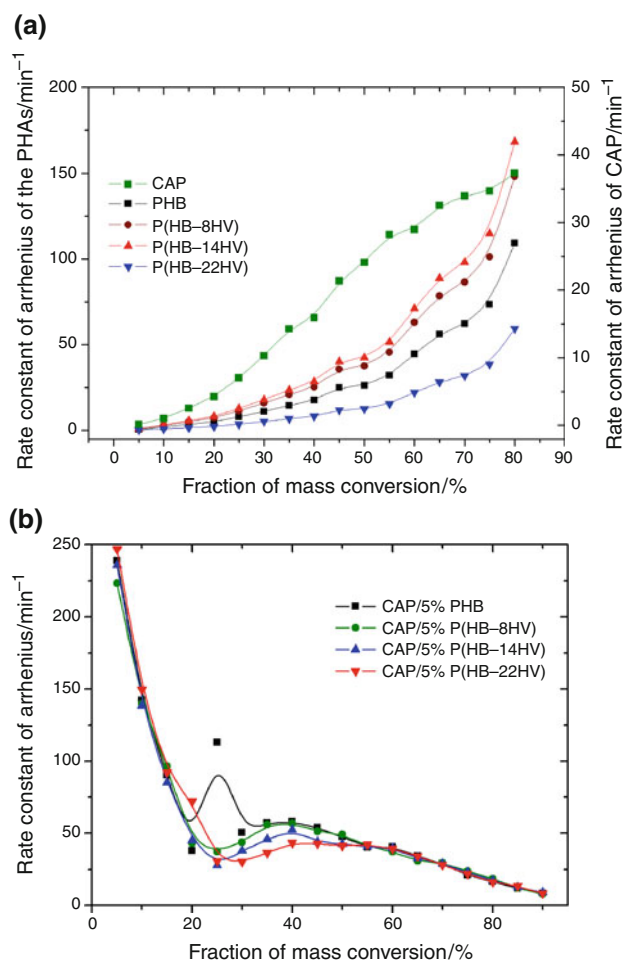


Fig. 11 Rate constant of Arrhenius versus fraction of mass conversion by Friedman method to **a** PHAs and CAP and **b** CAP/5% P(HB–HV) blends

interfaces make the formation of nuclei possible such that both the polymeric ones are degraded. This results in a large variation in the levels of E_a for mass conversion lower than 30%, as observed in the relationship of the activation energies on the fraction mass conversion.

An increase in the levels of activation energy was observed in the blends for the first step of thermal degradation. An improvement in the activation energy values on the CAP/PHAs blends can be explained by the profile of the reaction rate of the Arrhenius. The reaction rate of the Arrhenius is more sensitive to the details of the thermal degradation reaction, and is related to the reactivity of the reaction [36]. The PHAs are controlled by the reaction model type sigmoid with the formation of much nucleus of reaction, whereby the reaction rate accelerates to a maximum, resulting in a decrease on the values of activation energy in course of the thermal degradation process. On the other hand, CAP is controlled by the dimensional diffusion with the formation of only the nucleus which diffuses for polymer, whereby this behavior does not permit the

acceleration of the reaction rate (Fig. 11a). In addition, lower intensities are observed for this parameter.

The formulation of the CAP/PHAs blends results in a decrease of reactivity of the thermal degradation process with a loss in the reaction rate (Fig. 11b) of the PHA phase, which results in an increase of the thermal stability of PHA phase when blended with CAP. Moreover, the CAP phase does not significantly modify the thermal stability in blends.

Conclusions

The thermal degradation of the PHAs investigated by TGA occurs in short temperature intervals. However, the addition of HV comonomer modified the profile of thermal degradation of the PHAs. The additions of the HV content in PHAs increased the activation energy necessary to dissociate the linkages of the interatomic mechanisms responsible for the thermal degradation process as well as reduce the reactivity of this process. The CAP is thermally more stable than the PHAs, whereby it was shown that the temperature interval was large for the thermal degradation process. When the PHAs were blended with CAP, the synergetic interaction of the components of the blend slightly improved the thermal stability of the PHAs. The activation energy necessary for the thermal degradation process of the PHA phase increased, particularly with regard to the PHAs with a higher HV content. The increase in the activation energy can be attributed to a reduction in the reactivity of the reaction promoted for CAP. The CAP modified the reaction model to the PHA phase, which would empirically be associated with the mechanisms of the reaction. The reaction model to the PHAs changed from acceleratory to diffusion, which would justify the improvement in the thermal stability of this phase as fewer reactive nuclei were formed. The HV content did not significantly modify the thermal stability of the CAP in the blends; it only slightly reduced the reactivity of this component.

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